THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

THERMAL DECOMPOSITION OF SYNTHETIC POLYMERS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

WILLIAM MILLER WOODARD

Norman, Oklahoma

1973

THERMAL DECOMPOSITION OF SYNTHETIC POLYMERS

APPROVED BY

C. M. Sliepcevich

Reed Welker

W. E. Brown

Chairman

Edward D. Christian

DISSERTATION COMMITTEE

ABSTRACT

The weight and energy changes associated with the thermal decomposition of polystyrene, polymethylmethacrylate, and polyvinyl chloride have been investigated. The weight loss kinetics were studied in a nitrogen atmosphere at heating rates of 10, 20, 40, 80 and 160°C/min. The energy changes were studied in a nitrogen atmosphere at 10, 20, 40 and 80°C/min.

Several techniques for obtaining kinetic parameters from the experimental weight loss data were discussed. Two of these data analysis methods were applied to the experimental data gathered here, and the results of the analysis were considered relative to their ability to predict the weight loss characteristics of the decomposition and their ability to reveal individual steps in the degradation mechanism.

The total energy changes occurring during the decomposition were measured using differential scanning calorimetry. The energy changes attributed to pyrolysis were separated from the sensible heat effects.

Dependence of a thermal decomposition reaction on heating rate was defined and examples of theoretical reactions were given to illustrate dependence and non-dependence

on heating rate. Using the energy and weight loss data obtained here the dependence of the degradation of polystyrene, polymethylmethacrylate, and polyvinyl chloride on heating rate were discussed.

ACKNOWLEDGMENTS

It is impossible of course to properly express the gratitude that is felt towards the individuals that have contributed to the completion of this work. To the few mentioned here and the many who are not, I am sincerely grateful.

Dr. C. M. Sliepcevich, George Lynn Cross Research Professor of Engineering, for providing the opportunity to conduct this research and for his constant interest and support.

Dr. J. R. Welker, Associate Director of the Flame Dynamics Laboratory, for his untiring assistance.

Dr. L. E. Brown, for his patience and help in many areas.

Dr. H. H. West, for his interest and concern.

Mr. P. A. Trimble, for his friendship.

Dr. M. L. McGuire, for his encouragement in beginning graduate study.

Dr. A. W. Aldag, Assistant Professor of Chemical Engineering, and Dr. S. D. Christian, Professor of Chemistry, for serving on my graduate committee.

Ms. B. T. Everidge, for the preparation of the manuscript.

To the National Defense Education Act, Phillips Petroleum Company, the National Science Foundation, and University Engineers, Inc., I am grateful for financial support. Computer time was provided by Merrick Computing Center of the University of Oklahoma.

And finally, it has been my family who have sacrificed the most. My parents, my wife, and my children furnished the incentive for this work. Without their encouragement and support there would have been little reason for its completion.

William M. Woodard

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Synthetic polymeric materials are rapidly replacing many natural substances for uses in the home, in industry, and in transportation. The hazards imposed by these synthetic polymers when exposed to fire or a fire type environment are subject to considerable speculation and study. Important areas of research in these studies include: the ignition and burning characteristics of the polymers, the manner in which the polymer degrades if it does not burn, the amount and toxicity of the products of decomposition, and ways to make the polymer more thermally stable. In each of these areas there is a great need for basic information on the reaction of polymeric materials to extreme thermal environments.

For the past several years, the Flame Dynamics Laboratory at the University of Oklahoma has been concerned with the investigation of fundamental physical and chemical properties of pyrolyzing woods. Prior to the work done at the Flame Dynamics Laboratory one of the major obstructions to the development of a successful model describing the pyrolysis process was a lack of data on the chemical kinetics of the degradation process. The progress made at this laboratory,

most notably in the areas of weight loss kinetics at high heating rates, energetics of degradation, and thermal conductivity determination, has led to the development of a successful model describing the transient temperature and density profiles of pyrolyzing wood (1, 2). Their work is now to be partially extended and partially expanded to the study of three synthetic polymers: polystyrene, polymethylmethacrylate (Plexiglas), and polyvinyl chloride.

One of the least understood aspects of the thermal degradation process is the determination of the amount of thermal energy absorbed or released during decomposition and the effect of heating rate on this process. A major objective of this study will be to quantify the energy changes associated with the degradation and the effect of heating rate on these energy changes. A second objective of this study will be to determine the actual kinetics of the thermal decomposition process, the weight losses and rates of weight loss, and again the effect of heating rate on these processes. Although there have been other studies on the weight loss kinetics of these materials, there is a great need for reliable methods of treating the kinetic data. Specifically, a need exists for a method of obtaining kinetic parameters that allows the decomposition reaction to be accurately modeled. The determination of reliable kinetic parameters will thus be the third major objective of this study.

The thermal degradation of polymeric materials is inherently an extremely complex process (9, 10, 11). The very nature of polymer molecules in a pure state is reason enough for this complexity; when added to the fact that almost all commercial polymers, whether by design or by fate, contain various impurities, the problem of their kinetic study becomes even more difficult. By far the major portion of work done in the field of polymer degradation has been done with the goal of uncovering the basic mechanisms of the degradation process. While a detailed, mechanistic study of the degradation process is far beyond the scope of this work, the studies done here constitute one of the many steps that must be understood before a description of the thermal degradation process can be completed.

CHAPTER II

EXAMINATION OF PROBLEM AND REVIEW OF PREVIOUS WORK

Polymer Degradation

Classically the term degradation means, as suggested by Grassie (9), a breaking down of chemical structure, and in terms of polymer chemistry, this degradation would seem to imply a decrease in molecular weight. In its broadest sense, degradation can be said to mean the deterioration of those properties of polymers which make them useful. Discoloration of polymers, for example, is normally thought of as degradation although in certain cases it may be caused by an increase in molecular weight. Many outside influences may lead to polymer degradation: extreme temperatures, mechanical stress, ultrasonic vibrations, high-energy radiation, light, oxidation, and microbiological attack. In this study only thermal degradation of synthetic polymers at high temperatures will be considered. The term degradation as used here will be restricted to mean the breaking down of the polymer molecule resulting in a weight loss.

In an inert atmosphere polymer molecules decompose, when exposed to high temperature, to give various combinations of volatile products and char. Wall states (21) that, in

general, vaporization phenomena can be divided into three categories depending on the particular step in the process that is rate controlling: 1) rate proportional to surface area, 2) rate proportional to surface area and inversely proportional to thickness, and 3) rate proportional to weight of sample. This third category applies to practically all polymer decompositions and specifically to the polymer studies made in this work. Polymer molecules are normally so large that they will not vaporize without first breaking down into smaller fragments. Chemical bonds must be broken and, regardless of the mechanism, the rate of volatilization is basically proportional to the rate of bond breakage. The number of bonds in a polymer molecule is directly related to the weight of the molecule, and as such the rate of weight loss is, ideally, proportional to the weight of the polymer.

The thermal degradation of a polymer sample involves a break in the main chain, or backbone, of the polymer molecule or the splitting off of side groups from the chain, or both. The breaks in the main polymer chain may occur at random or they may occur primarily at the chain ends. In some instances both types of chain scission occur. In the random process the molecular weight of the polymer sample will drop rapidly and continuously with the extent of reaction, and a wide variety of degradation products may be formed. In the terminal process, although the molecular weight will

drop, it will not drop nearly as rapidly as with random scission, and large amounts of monomer may be formed.

Madorsky states (3) that for a full understanding of the mechanism involved in the thermal degradation of organic polymers, it is necessary to know, among other facts, three fundamental characteristics: the change in molecular weight as a function of temperature and extent of degradation, the qualitative and quantitative composition of the volatile and nonvolatile products of degradation, and the rates and activation energies of the degradation process. While the determination of mechanism is not of primary concern in this work, it is felt that a significant contribution is made in the last two of the three areas mentioned.

Thermal Analysis

The study of the thermal degradation of synthetic polymers requires knowledge and practice in the specialty known as thermal analysis. In this specialty the two methods of analysis most commonly employed are thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The general characteristics of these two methods will be presented here. Specific details of the experimental work conducted for this dissertation will be discussed in a later chapter.

TGA, as the name suggests, involves measuring the changes in weight of a substance as it is heated. A balance mechanism to record changes in sample weight and a heating

mechanism to provide the proper thermal environment are the major instruments required for this type of analysis. Normally a sample is either raised as rapidly as possible to a prescribed temperature and held there (isothermal gravimetric analysis), or the temperature is increased at a linear rate (dynamic thermogravimetric analysis) until decomposition is complete. There are several problems that apply to some degree to all TGA investigations. These problems normally depend on the particular instruments and techniques used.

Ideally the polymer sample should be kept small enough to make an assumption of uniform temperature valid. If the sample is not heated uniformly throughout, the problem of determining the temperature at which the reaction is occurring becomes very complex. In early TGA work, this temperature determination was a major problem due to the relatively large samples required to measure weight changes accurately. Today, however, where sample sizes on the order of 1-2 mg are quite common, this problem has become much less significant. In isothermal studies, especially at higher temperatures, a major problem is instantaneously raising the sample to the desired temperature. If this cannot be done satisfactorily, a significant portion of the reaction may have occurred by the time the sample reaches the temperature of interest. One of the major areas of concern in the past, and most probably still the major problem assocaited with TGA, is the measurement of the temperature of the sample undergoing decomposition. For

obvious reasons, when dealing with a balance that can detect weight changes of 10^{-5} gm, it is undesirable to place a thermocouple in contact with the sample in the sample pan. The most common solution to this problem has been to place a thermocouple as near as possible to the sample without interfering with the weighing mechanism. This procedure still leaves the question of how the temperature measured by the thermocouple relates to the temperature of the sample in the pan. Perhaps the only truly original contribution made in this area was developed by the Perkin-Elmer Corporation. They make use of the magnetic transition temperatures of various metal alloys in a unique method of temperature calibration with their TGA apparatus.

The second area of concern in thermal analysis has to do with the energy changes associated with polymer degradation. DTA is by far the most common technique used for this type of study. DTA makes use of the fact that all polymers to a greater or lesser degree undergo some energy changes while undergoing thermal decomposition. In theory DTA supplies two sample holders, one containing the polymer sample and one a reference, with a constant thermal environment, while monitoring the temperature of each pan individually (Figure II-1a). As the sample decomposes, its temperature will change relative to the reference pan, depending on the amount and direction of the energy changes associated with the degradation. The area under the DTA curve (Figure II-1b) is theoretically

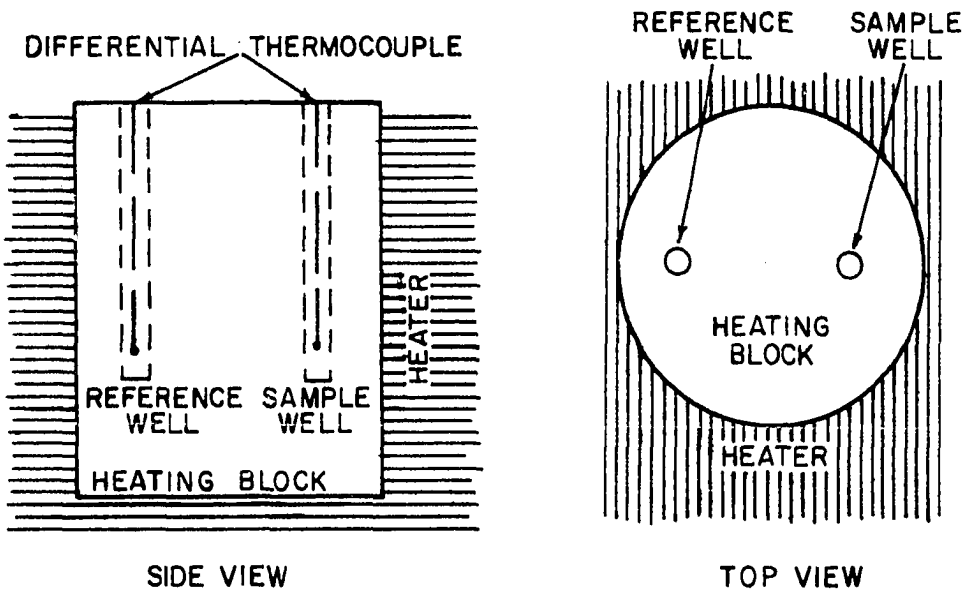

Figure II-1a. Typical DTA Configuration.

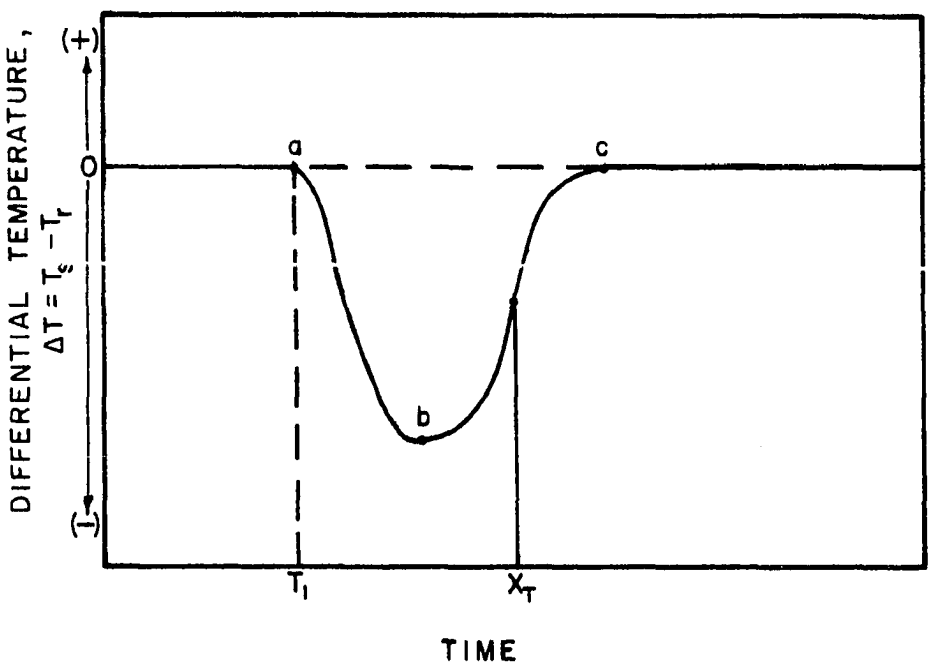

Figure II-1b. Idealized DTA Recording of an Endothermic Transition.

proportional to the amount of energy absorbed or released by the sample during decomposition. DTA is adequate for indicating the temperatures at which degradation occurs and for indicating the qualitative nature of the energy changes. It has one very serious shortcoming, however, that makes it unsuitable for quantitative measurements: it must be assumed with DTA that the heat transfer characteristics of the sample and sample holder assembly do not change as the sample decomposes. DTA has no method of detecting changes in heat transfer and consequently no method of accounting for them. As demonstrated by Havens (1), very small changes in a property, such as emissivity, that affect heat transfer characteristics may cause major errors in quantitative energy data.

A technique closely related to DTA that is the only successful method available for this type of energy studies is differential scanning calorimetry (DSC). DSC also involves the use of two sample pans, one containing the polymer sample being studied and one reference pan. DSC attempts to keep the two pans at the same temperature, through the use of a feedback control circuit, while measuring the difference in electrical energy requried to maintain equal temperature. Although it is not always possible to eliminate or account for changes in heat transfer characteristics with the DSC, it is very obvious when they occur. The details of DSC operation will be discussed in greater detail later.

The Thermal Decomposition of Polystyrene

Polystyrene was perhaps the first of the synthetic polymers to undergo a systematic study of its thermal decomposition properties (4) and has probably been subject to more study than any single synthetic polymer. Almost without exception the studies reported on polystyrene degradation have as their primary goal the determination of the fundamental steps in the decomposition process. As mentioned previously this type of detailed, mechanistic study is not one of the objectives here; however, of necessity these studies will be included in this review.

Before continuing with the discussion of polystyrene degradation, an explanation of the terms "order" and "activation energy" is necessary. It appears that in the past, perhaps too much significance has been attached to these terms. These terms arise as constants in an equation of the classical Arrhenius type

$$dc/dt = A\, e^{-E/RT}\, (c)^n \qquad \text{(II-1)}$$

where E is the activation energy, n the order of the reaction, A the frequency factor, and C a concentration term. As originally developed by Arrhenius, Equation II-1 was simply an empirical equation; it has been very successful in fitting chemical kinetic reaction rate data. It will be shown in a later section that the particular values obtained for these

constants can depend on the method used in applying Equation II-1 to experimental data. For the present it is suggested that the reader keep in mind where these terms originated and be warned against attaching too much meaning to them. A detailed look at this equation and methods used for applying it to experimental data will be reserved for a later section. Where possible, an explanation of how the individual investigators covered in this review obtained their numerical values for n and E will be given.

Jellinek, in a series of papers published in 1948 and 1949 (5, 6, 7), studied the thermal decomposition of polystyrene, under vacuum conditions, over a range of temperatures from 248° to 400°C. All experiments were carried out isothermally with sample sizes of 0.1 to 0.5 gms. A zero order reaction was assumed for the decomposition, and an activation energy of 44.7 kcal/mole was calculated based on the rate of monomer formation. A detailed mechanism was postulated for polystyrene decomposition, initiated by "weak links" in the polymer chains due to the presence of small amounts of chemically bound oxygen. Jellinek assumed a zero order for his reaction. The rate of reaction was then expressed as

$$dx/dt = Ae^{-E/RT} \qquad \text{(II-2)}$$

where x was the amount of monomer produced in grams. The amount of monomer formed was plotted as a function of time at

each temperature studied, and the portion of the curve that followed a straight line was used to calculate the rate constant k, where

$$k = Ae^{-E/RT} \qquad \text{(II-3)}$$

The log of each calculated rate constant was then plotted as a function of 1/T and the activation energy determined from the slope of the line obtained.

In 1952 Madorsky (8) reported the results of a study on the thermal decomposition of polystyrene and polyethylene under vacuum conditions. His experiments were carried out isothermally over a temperature range of 335° to 365°C. The sample size used for this series of tests ranged from 5 to 7 mg. One important result presented in his paper was that for three samples of widely varying molecular weight, from 106,000 to 584,000, the activation energy calculated for the decomposition reaction was a constant. Madorsky also mentioned that the activation energy should not be considered as referring to any one particular reaction taking place in the process of thermal degradation, but should be looked upon as a composite value of several reaction mechanisms. He inferred from his results that polystyrene degrades at these conditions primarily at the molecular chain ends, but that some random degradation takes place simultaneously.

Madorsky assumed a zero order reaction in his calculation of activation energies. Unlike Jellinek, however, he

based his calculations on the rate of weight loss of the polymer samples

$$- dw/dt = Ae^{-E/RT} \qquad \text{(II-4)}$$

where w is a normalized sample weight. He did not obtain a single rate constant at each temperature but calculated individual rate constants at each of three conversions: 0 percent, 25 percent and 50 percent. The log of each rate constant was then plotted at each conversion as a function of 1/T, and the activation energies were determined from

$$-E = 2.3\ R \frac{d(\log\ k)}{dT} \qquad \text{(II-5)}$$

The activation energy corresponding to the initial rate of weight loss (0 percent conversion) was 58 kcal/mole; at 25 percent conversion it was 56 kcal/mole; and at 50 percent conversion, 54 kcal/mole.

Anderson and Freeman (12) investigated the decomposition kinetics of polystyrene using dynamic thermogravimetric analysis. Their studies were carried out under vacuum conditions, and the 100 mg samples were heated from ambient temperature to 500°C at a rate of 5°C/min. The polystyrene samples, of average molecular weight 360,000, began losing weight at 320°C. The maximum rate of weight loss occurred at 390°C, and the reaction went to completion at 430°C with a 99 percent loss in weight. The kinetics were evaluated by the method of Freeman and Carroll (13), which is based on the expression

$$\Delta \log (dw/dt) = n \Delta \log W_r - (E/2.3R)\Delta(1/T) \qquad \text{(II-6)}$$

where dw/dt is the rate of weight loss, n is the order of reaction, E is the activation energy, and W_r is the initial sample weight minus the weight of the sample at the point where dw/dt is taken. $\Delta(1/T)$ was held constant and $\Delta \log(dw/dt)$ plotted against $\Delta \log W_r$. The order of reaction was calculated from the slope, and the activation energy was calculated from the intercept at $\Delta \log W_r = 0$. A plot of their data made in this manner is shown in Figure II-2. The points falling on the straight line represent approximately 80 percent of the total weight loss. In this range a reaction order of one was calculated, and an activation energy of 60 kcal/mole was obtained. A temperature dependency plot was made by Anderson and Freeman for the initial 10 percent of the decomposition reaction where the rate of reaction was plotted against 1/T. From this plot they concluded the low temperature stage of the reaction was of zero order and calculated an activation energy of 46 kcal/mole. They stated that the results indicated two mechanisms of degradation, one predominant over low temperatures up to 370°C and the other at high temperatures.

Anderson and Freeman went on to say their results resolved the conflicting values of activation energy reported by Jellinek (44.7 kcal) and Madorsky (54-58 kcal). They stated that Jellinek studied the pyrolysis below 340°C and Madorsky above 340°C, and since the results of their

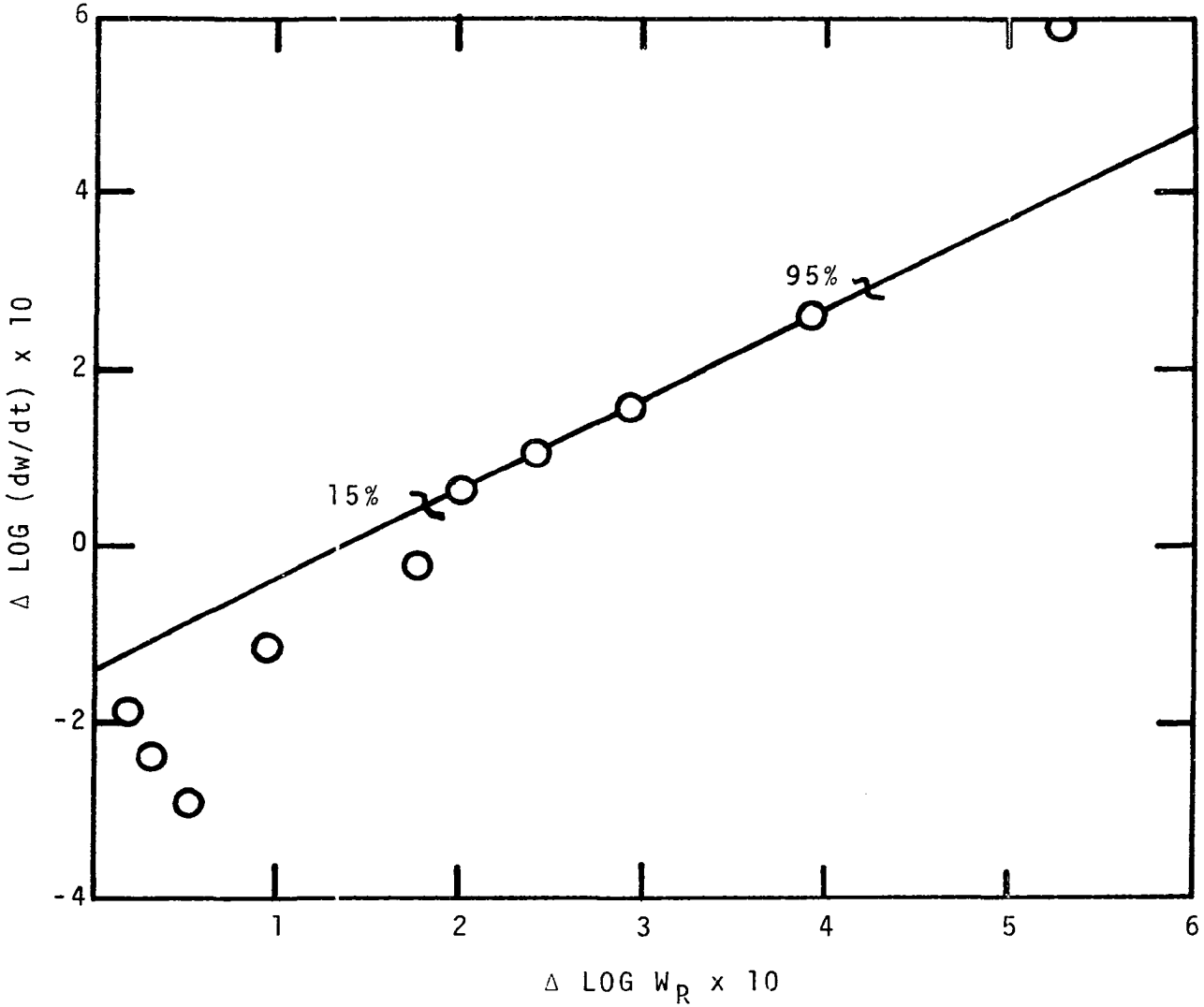

Figure II-2. Kinetics of the Thermal Degradation of Polystyrene. Data of Anderson and Freeman. (13).

investigation indicated the activation energy is a function of temperature, the results of Jellinek and Madorsky were to be expected. While the results of Jellinek and Madorsky are resolvable, there exist some major discrepancies in the reasoning of Anderson and Freeman. In the first place their statement that Jellinek studied the pyrolysis below 340°C and Madorsky above 340°C is very inaccurate. The data taken by Jellinek (7), upon which he based his calculation of activation energy, were taken at temperatures of 348°, 364°, 380° and 398°C. The actual temperatures studied by Madorsky (8) were 335°, 340°, 345°, 350°, 355°, 360° and 365°C. The temperature ranges studied were roughly the same, and, in fact, Jellinek actually studied at slightly higher temperatures than Madorsky. These facts certainly eliminate the reasoning Anderson and Freeman used to explain the different activation energies. The confusion about the temperature ranges studied most probably came as the result of an earlier paper published by Jellinek (5). In this paper he did study the temperature range from 248°-340°C. It was, however, definitely not this latter data but that mentioned above used to calculate the 44.7 kcal/mole activation energy.

There is a very reasonable explanation that to some extent shows the consistency of the data reported by these three different investigators. Jellinek's value of activation energy was based on the rate of monomer formation and not on the rate of total weight loss. It is generally agreed that

in the early stages of polystyrene decomposition monomer is the principal degradation product. Jellinek's calculation of activation energy was most likely based on the earlier stages of decomposition and corresponds with the value of 46 kcal/mole calculated by Anderson and Freeman. Madorsky used the portion of his weight loss curves from roughly 10 percent to 75 percent decomposition to calculate his activation energies. Even though he assumed a zero order of reaction, his values of activation energy, ranging from 54 to 58 kcal/mole, are in general agreement with the value of 60 kcal/mole calculated by Anderson and Freeman using a first order reaction. In the investigations reported here, it was found that the activation energy can be relatively insensitive to an assumed reaction order. It might also be mentioned that Anderson and Freeman were a bit hasty in their conclusion of the temperature dependency of the decomposition reaction with the limited amount of data used. While at this point their statements cannot be absolutely refuted, there are certainly other explanations possible.

Wall reported in 1966 (14) a detailed theoretical and experimental study on polystyrene degradation. His experimental studies were carried out isothermally, under vacuum conditions, and over a very wide range of molecular weights. Sample sizes were between 5 and 10 mg. The temperature range studied was from approximately 300°C to 365°C. Although no details were given, it is assumed that activation energies

were calculated using a technique similar to Madorsky's. Zero-order kinetics were assumed, and the calculated activation energies in kcal/mole, with the corresponding molecular weights given in parentheses were 24 (3,500), 35 (7,000), 42 (14,000), 47 (24,500), 48 (30,000), 49 (45,000), 49 (64,000), and 49 (2,000,000). These figures show the activation energy to be a function of molecular weight at very small values of molecular weight.

Wegner and Patat (15) studied the thermal degradation of polystyrene taking extreme care to obtain pure samples for investigation and to degrade them under clean conditions. One hundred mg samples were decomposed isothermally, under vacuum conditions, at temperatures from 200°C to 325°C. The authors said the decomposition was a first order reaction based on their molecular weight determinations. An activation energy of 48 kcal/mole was calculated and, although few details were given on the method used to calculate the activation energy, it seemed to be based on a zero-order reaction. The results of this investigation of polystyrene decomposition differed significantly from other studies in the variation of molecular weight with extent of degradation. In previous studies a rapid initial drop in molecular weight was observed, followed by a gradual decrease in the second stage. Wegner and Patat observed an almost linear drop in molecular weight over the entire decomposition range.

The preceding review is felt to be representative, although certainly not exhaustive, of the work done to date on polystyrene decomposition. The literature available on polystyrene is quite extensive with several reviews available (16, 17, 18, 19, 20) for those interested. Table II-1 is a partial summary of the kinetic parameters obtained by different investigators for the thermal decomposition of polystyrene.

From the survey of the literature the following observations were made. Although it is generally recognized that dynamic thermogravimetric analysis yields more information than isothermal TGA, the vast majority of studies of polystyrene have been made using isothermal techniques. Where dynamic TGA has been used, generally only one heating rate is studied; there is no systematic study available on the affects of heating rate on the thermal decomposition of polystyrene. Very little effort has gone into the determination of kinetic parameters from the thermal decomposition data. In most instances a reaction order is simply assumed and an activation energy calculated based on this assumed order. Nowhere has an attempt been made to back calculate weight loss curves and compare them with experimental data. There are no energy data published dealing with polystyrene decomposition. There are DTA studies available (23), but these were only used to calculate kinetic parameters; no attempt was made to quantify the energy changes associated with degradation.

TABLE II-1

KINETIC PARAMETERS FOR THERMAL DECOMPOSITION OF POLYSTYRENE

Investigator	Method	Sample Size	Temperature Range (Heating Rate)	Order	Activation Energy (kcal/mole)
Jellinek	Isothermal TGA	0.1-0.5 grams	348°C-398°C	0 (assumed)	44.7
Madorsky	Isothermal TGA	5-7 grams	335°C-365°C	0 (assumed)	54-58
Anderson and Freeman	Dynamic TGA	100 mg	(5°C/min)	1 (calculated) 0 (assumed)	60 (15-95% decomp.) 46 (0-10% decomp.)
Wall, et al.	Isothermal TGA	5-10 mg	300°C-365°C	0 (assumed)	47-49
Wegner and Patat	Isothermal TGA	100 mg	200°C-325°C	?	48
Reich	Dynamic DTA	9-18 mg	8°C/min	0.97 - 1.3	73-90

The Thermal Decomposition of Polymethylmethacrylate (Plexiglas)

Madorsky (24) studied the thermal degradation of seven synthetic polymers including polymethylmethacrylate (PMMA). The studies were done isothermally, under vacuum conditions, in a temperature range of 240°C to 325°C. Sample weights ranged from 5 - 7 mg. Two grades of this polymer were investigated; one of low molecular weight (150,000) and one of high molecular weight (5,100,000). The low molecular weight samples were decomposed at temperatures of 240°C, 250°C, 260°C, and 270°C. They had high initial rates of decomposition, and volatilization came essentially to a complete stop, at these temperatures, at 40 to 47 percent weight loss. To calculate the activation energy of the reaction, a plot was made of the rate of weight loss as a function of percent weight loss (Figure II-3). The straight line portion of the curves, covering at most a 15 percent weight loss range, were extrapolated to 0 percent weight loss, and this value was then said to be the initial rate of volatilization. At the onset of decomposition the initial rate is equal to the Arrhenius rate constant (Equation II-3), and from a plot of k as a function of 1/T, the activation energy may be determined. For the low molecular weight PMMA, the activation energy was 33 kcal/mole. As for order, Madorsky simply said that the rate curves resembled those of a first order reaction.

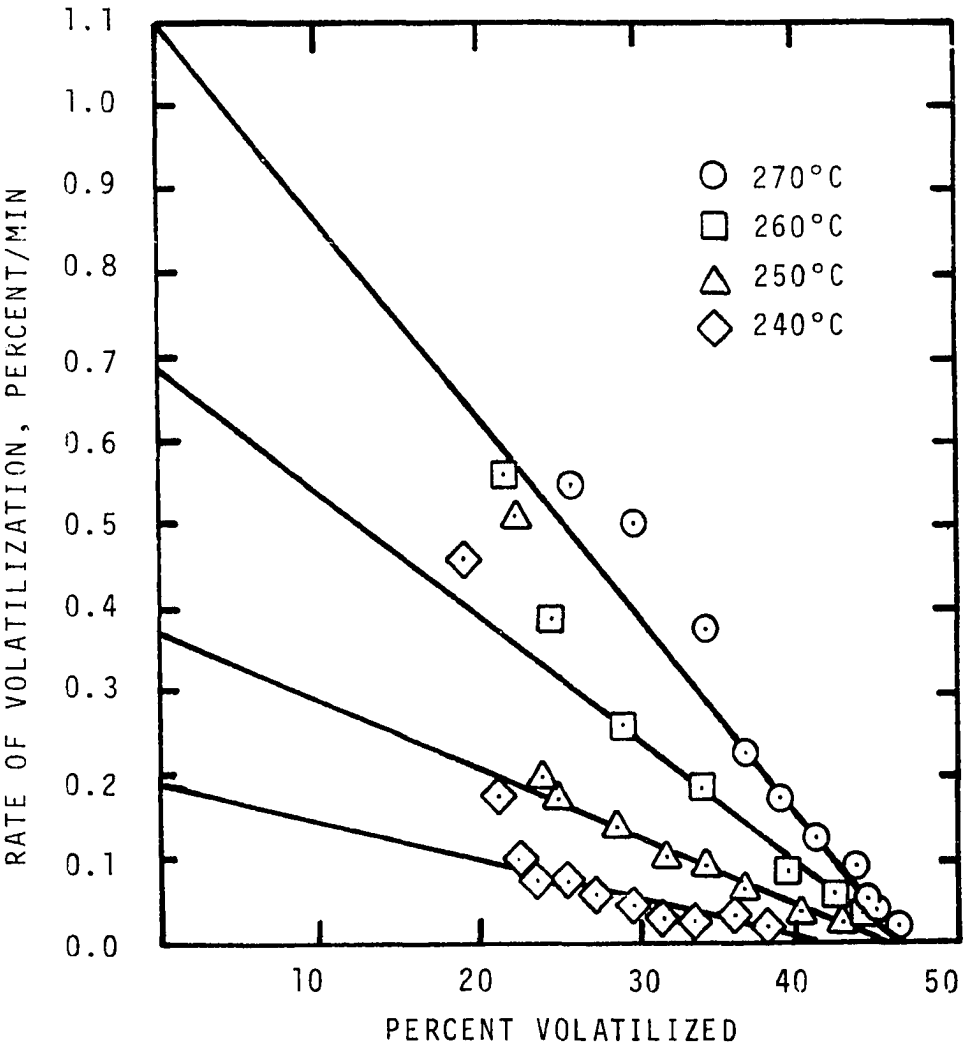

Figure II-3. Rates of Volatilization of Polymethylmethacrylate as a Function of Percent Volatilization. Data from Madorsky (24).

The high molecular weight PMMA samples were degraded at somewhat higher temperatures: 310°, 315°, 320°, and 325°C. The initial rate of weight loss was determined as for the low molecular weight samples, although at these temperatures the PMMA was 100 percent volatilized and the straight portion of the curve covered only approximately 40 percent of the degradation range. The activation energy was found to be 55 kcal/mole.

Jellinek and Clark (25, 26) developed a new technique for studying the thermal decomposition of polymers and applied it to the study of PMMA. The technique was developed to study reactions that involved high volatilization rates and has been somewhat outdated by the TGA equipment now available. The instrument developed by these investigators is called a quartz spoon gage and follows the extent of reaction by continuously recording the pressure produced by the volatile products of decomposition. Experimental results are given in moles of gas produced as a function of time. In order to convert these results to weight loss, it is necessary to know the degradation products. PMMA degrades to nearly 100 percent monomer and was thus an ideal polymer to study on this apparatus.

Samples of polymer 20 mg in weight were degraded over a range of temperatures from 275° to 400°C. The rate of volatile production, dn/dt, was plotted against the number of moles of gas produced at each temperature studied.

Assuming the decomposition is first order, the slope of this curve, d(dn/dt)/dn, at any point will give the Arrhenius rate constant at the particular conversion. If the log of the rate constant, at a constant value of conversion, is plotted versus 1/T, the slope of the line obtained will be the activation energy. Jellinek and Clark presented activation energies calculated at four values of conversion: 20 percent, 40 percent, 60 percent and 80 percent. An activation energy of 26 kcal/mole was obtained at 20 percent conversion, and 49.5 kcal/mole was obtained at the other three conversions.

Wilson and Hamaker (27) combined a mass spectrometer with a thermal gravimetric analysis unit to study the decomposition of several polymeric materials. The mass spectrometer allowed the products of the decomposition to be analyzed continuously throughout the degradation range. PMMA samples 5 to 25 mg in weight were degraded, under vacuum conditions, using dynamic TGA at a heating rate of 1°C/min. The upper temperature limit of the system was 435°C. Kinetic parameters were obtained based on the mass spectrometer data. Two distinct stages of weight loss were indicated for PMMA degradation. The first stage was determined to be first order with an activation energy of 13.1 kcal/mole. The second stage was also said to be first order, and an activation energy of 44.9 kcal/mole was calculated.

The thermal degradation of polystyrene or polymethylmethacrylate is a classic example of the problems associated

with TGA data analysis. In all instances the decomposition of polystyrene gives a smooth weight loss curve and a smooth rate of weight loss curve. Hopefully these results would indicate only one primary weight loss step. However, the products from the thermal degradation of polystyrene, along with the results of a detailed kinetic data analysis, indicate that polystyrene decomposition is more complex than this. PMMA, on the other hand, in all studies reported, degrades to 100 percent monomer. This again might lead to the hope for only one weight loss mechanism. The TGA curves for PMMA decomposition indicate that this is not the case. As will be shown in the next section, selecting the proper method of kinetic data analysis can be a very necessary step in resolving the details of a thermal degradation reaction.

Kinetic Analysis of TGA Data

The significance of kinetic parameters obtained from the analysis of TGA data is subject to a great deal of speculation. A great variety of techniques for extracting kinetic parameters are currently in use. Many of these techniques are presented, and widely used, with little or no discussion of their applicability or of the assumptions inherent in their use. Reviews are available on kinetic analysis (28, 30, 31), but for the most part the analytical techniques are discussed from a theoretical point of view and compared using idealized data.

It has been the general impression in reviewing the field of polymer decomposition that in many instances little attention is given to the method of obtaining kinetic parameters from TGA data while very detailed mechanistic descriptions are drawn from this same data. In the discussion that follows, some of the problem areas are illuminated, and some specific problems in TGA data analysis are outlined. Certainly all of the questions that will arise in this discussion are not answered. However, it is important to be aware of these questions that all too often are simply ignored.

The first problems arise, unfortunately, with the presentation of the equation which, in one form or another, has without exception been applied to polymer decompositions:

$$\frac{dc}{dt} = Ae^{-E/RT} f(c) \qquad \text{(II-7)}$$

In this equation the rate of change with respect to time of a concentration term, c, is related to a function of concentration, f(c), by a rate constant of the Arrhenius type, $Ae^{-E/RT}$. A theoretical justification for the application of this equation to polymer decompositions has apparently never been presented. The success of this equation from a practical standpoint, when applied to more traditional chemical reactions, along with the universal use of it in the past for polymer degradation studies will serve as justification for its continued consideration.

It has been the general impression in reviewing the field of polymer decomposition that in many instances little attention is given to the method of obtaining kinetic parameters from TGA data while very detailed mechanistic descriptions are drawn from this same data. In the discussion that follows, some of the problem areas are illuminated, and some specific problems in TGA data analysis are outlined. Certainly all of the questions that will arise in this discussion are not answered. However, it is important to be aware of these questions that all too often are simply ignored.

The first problems arise, unfortunately, with the presentation of the equation which, in one form or another, has without exception been applied to polymer decompositions:

$$\frac{dc}{dt} = Ae^{-E/RT} f(c) \qquad \text{(II-7)}$$

In this equation the rate of change with respect to time of a concentration term, c, is related to a function of concentration, f(c), by a rate constant of the Arrhenius type, $Ae^{-E/RT}$. A theoretical justification for the application of this equation to polymer decompositions has apparently never been presented. The success of this equation from a practical standpoint, when applied to more traditional chemical reactions, along with the universal use of it in the past for polymer degradation studies will serve as justification for its continued consideration.

In the examination of Equation II-7 one of the first questions to arise is the definition of a concentration term. Polymers generally contain molecules with wide variations in molecular weight. Even if there initially is a monodisperse polymer, with the onset of decomposition the molecular weight changes and normally does so continuously throughout the reaction. Thus, even if it were possible to define the molecular weight continuously through the degradation, the use of the traditional definitions of concentration in Equation II-7 would be very difficult. Wall (21) has given, based on intuitive arguments, reasons for expressing this equation in terms of the weight of the polymer sample

$$- \frac{dw}{dt} = Ae^{-E/RT} f(w) \qquad \text{(II-8)}$$

where w is the instantaneous weight of the sample. His reasoning for this selection was presented in the earlier section on polymer degradation. Since the rate of degradation expressed in Equation II-8 is now a direct function of sample size, some type of normalized weight is needed that will give a consistent basis for comparing polymer degradation studies. The most convenient way of doing this, and one of the most widely used, is to express the weight in terms of the fractional weight remaining:

$$W = \frac{w - w_f}{w_o - w_f} \qquad \text{(II-9)}$$

where W is the fractional weight remaining, w is the instantaneous sample weight, w_f the final or residue weight, and w_o is the initial sample weight. Substituting this into Equation II-8 gives

$$-\frac{1}{w_o - w_f}\frac{dw}{dt} = Ae^{-E/RT} f\left(\frac{w - w_f}{w_o - w_f}\right) \qquad \text{(II-10)}$$

The analysis techniques discussed in this section will basically attempt to apply Equation II-10 to polymer decomposition data.

The techniques used to extract kinetic parameters from weight loss data are divided into two broad classes: those using differential treatments of the data and those using integral treatments. Differential methods attempt to apply Equation II-10 directly, while the integral methods use an integrated form of the equation. The differential methods are the easiest to apply and have been by far the most widely used. In the past the only objection to the differential as opposed to the integral techniques was the error introduced with the graphical differentiation of the weight loss data. With the use of the automatic differentiating equipment now available, this objection has to a great extent been overcome. The following discussion is confined to the differential techniques.

In the treatment of isothermal TGA data the approach to the determination of kinetic parameters has been basically the same in all the investigations studied. The equation

$$-\frac{1}{w_o - w_f}\frac{dw}{dt} = Ae^{-E/RT}\ (W)^n \qquad \text{(II-11)}$$

is assumed to apply to the degradation reaction. The weight functionality, f(W), of Equation II-10 has been assumed to be of the order type, $f(W) = (W)^n$, where n is called the reaction order. Generally, n is simply assumed to be either 1 or 0. With this value of n, and knowing the weight loss and rate of weight loss as a function of time from experimental data, the rate constant k (Equation II-3) may be calculated at any point during the decomposition. Ideally, if a one-step weight loss mechanism occurs and if the proper value of n was chosen, k would be constant for all values of W. Practically, however, this result does not occur, and the calculated k's are compared at constant values of W over the range of temperatures studied. At a constant value of W the log of each calculated rate constant is plotted versus 1/T at each isothermal temperature studied.

$$\log k = \log A - E/2.3RT \qquad \text{(II-12)}$$

As can be seen from Equation II-12, the slope of this plot, assuming it is a straight line, enables the calculation of E, and the intercept gives log A. If E changes significantly over the range of decomposition, it may be difficult to attach any real significance to it. This could, however, be a good indication that more than one weight loss mechanism is

operative, or it could mean simply that a poor choice was made in the assumed reaction order.

The best opportunity for obtaining a meaningful parameter from this type of analysis is in the early stages of decomposition. In the early stages, as W approaches 1, the rate constants are relatively insensitive to the assumed reaction order whereas in the later stages they are not. If a plot of k is made as a function of W and extrapolated to W = 1, at each temperature studied, the initial rate constants may be obtained. From these initial rate constants an activation energy may be calculated for the onset of decomposition. It is still necessary to know, however, that only one weight loss mechanism is operative in order to attach any direct meaning to E. One of the major drawbacks to the calculation of this initial E is that, especially when the polymer degrades at a high initial rate, in isothermal studies the data in the early states of decomposition are the most unreliable.

The same information that is obtained from this type of analysis using several isothermal TGA curves may be obtained from a single dynamic TGA curve, which is one major advantage of dynamic TGA. If a reaction order is again assumed, rate constants may be calculated as before at various values of W. Since the temperature has been changing continuously through the course of the reaction, a series of k's and their corresponding temperatures from which the activation energy can be calculated is now available from a single TGA

operative, or it could mean simply that a poor choice was made in the assumed reaction order.

The best opportunity for obtaining a meaningful parameter from this type of analysis is in the early stages of decomposition. In the early stages, as W approaches 1, the rate constants are relatively insensitive to the assumed reaction order whereas in the later stages they are not. If a plot of k is made as a function of W and extrapolated to W = 1, at each temperature studied, the initial rate constants may be obtained. From these initial rate constants an activation energy may be calculated for the onset of decomposition. It is still necessary to know, however, that only one weight loss mechanism is operative in order to attach any direct meaning to E. One of the major drawbacks to the calculation of this initial E is that, especially when the polymer degrades at a high initial rate, in isothermal studies the data in the early states of decomposition are the most unreliable.

The same information that is obtained from this type of analysis using several isothermal TGA curves may be obtained from a single dynamic TGA curve, which is one major advantage of dynamic TGA. If a reaction order is again assumed, rate constants may be calculated as before at various values of W. Since the temperature has been changing continuously through the course of the reaction, a series of k's and their corresponding temperatures from which the activation energy can be calculated is now available from a single TGA

experiment. From a plot of log k versus 1/T, a value of -E/2.3R for the slope of the line is obtained, and the intercept is log A. If this plot gives a curved line, an indication is given that more than one weight loss mechanism is operative over the degradation range, or again a possibility that the assumed reaction order is wrong. This technique may be applied at a number of different heating rates and, although the kinetics may not be definable, changes in kinetics with heating rate may be observed.

A slight variation on the above technique may enable a single set of kinetic parameters to be obtained over the complete decomposition range. To accomplish this the logarithm of Equation II-11 is taken

$$\log \left(-\frac{1}{w_o - w_f} \frac{dw}{dt}\right) = \log A - E/2.3RT + n \log W \qquad \text{(II-13)}$$

Rearranging this slightly,

$$\log \left(-\frac{1}{w_o - w_f} \frac{dw}{dt}\right) - n \log W = \log A - E/2.3RT \qquad \text{(II-14)}$$

Everything on the left side of Equation II-14 is known from experimental data with the exception of n. If it is possible to obtain a single set of kinetic parameters over the entire decomposition range, and if the "best" value of n is known, a plot of the left side of Equation II-14 versus 1/T should give a straight line. If a one-dimensional search is done with n as the optimization parameter, the "best" value of n

is defined as the one that gives the best straight line when the left side of Equation II-14 is plotted against 1/T. E may be calculated from the slope of the line and log A is the intercept. The results of an application of this technique, as applied to the decomposition of a polystyrene sample heated at 20°C/min, are shown in Figure II-4. In Figure II-4 it is noticed at the lower temperatures, which is the low conversion range, all values of n converge to the same straight line. Many authors have come to the conclusion from examining their data in the low conversion range that zero order kinetics are indicated. Figure II-4 shows clearly that the kinetics become very insensitive to order in the low conversion range and that the presumption of any order from data only in this range could be very misleading.

One of the prerequisites for the successful application of the preceeding technique is that the rate of weight loss curve be smooth, exhibiting only one maximum, such as that of polystyrene shown in Figure II-5. Many common synthetic polymers exhibit this type of decomposition behavior. Although a single set of kinetic parameters that apply over the complete degradation range may often be obtained using this method, there is still absolutely no guarantee that these parameters have any real significance as applied to elementary decomposition steps. Polystyrene is a good example. As will be shown in a later chapter, the decomposition of polystyrene may be very successfully modeled over a wide range of heating

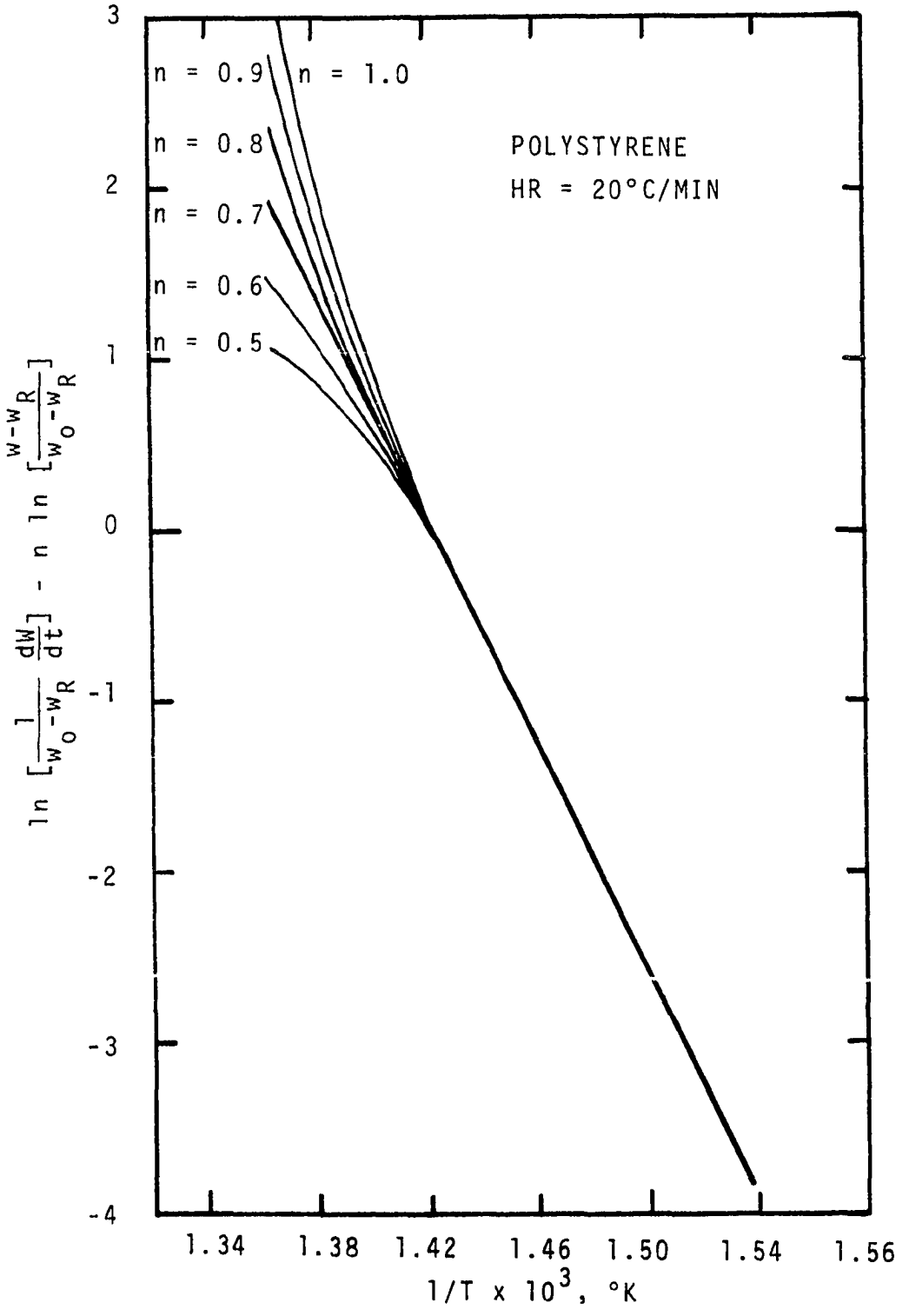

Figure II-4. Determination of n from Equation II-14 Polystyrene Decomposition at a Heating Rate of 20 °C/min.

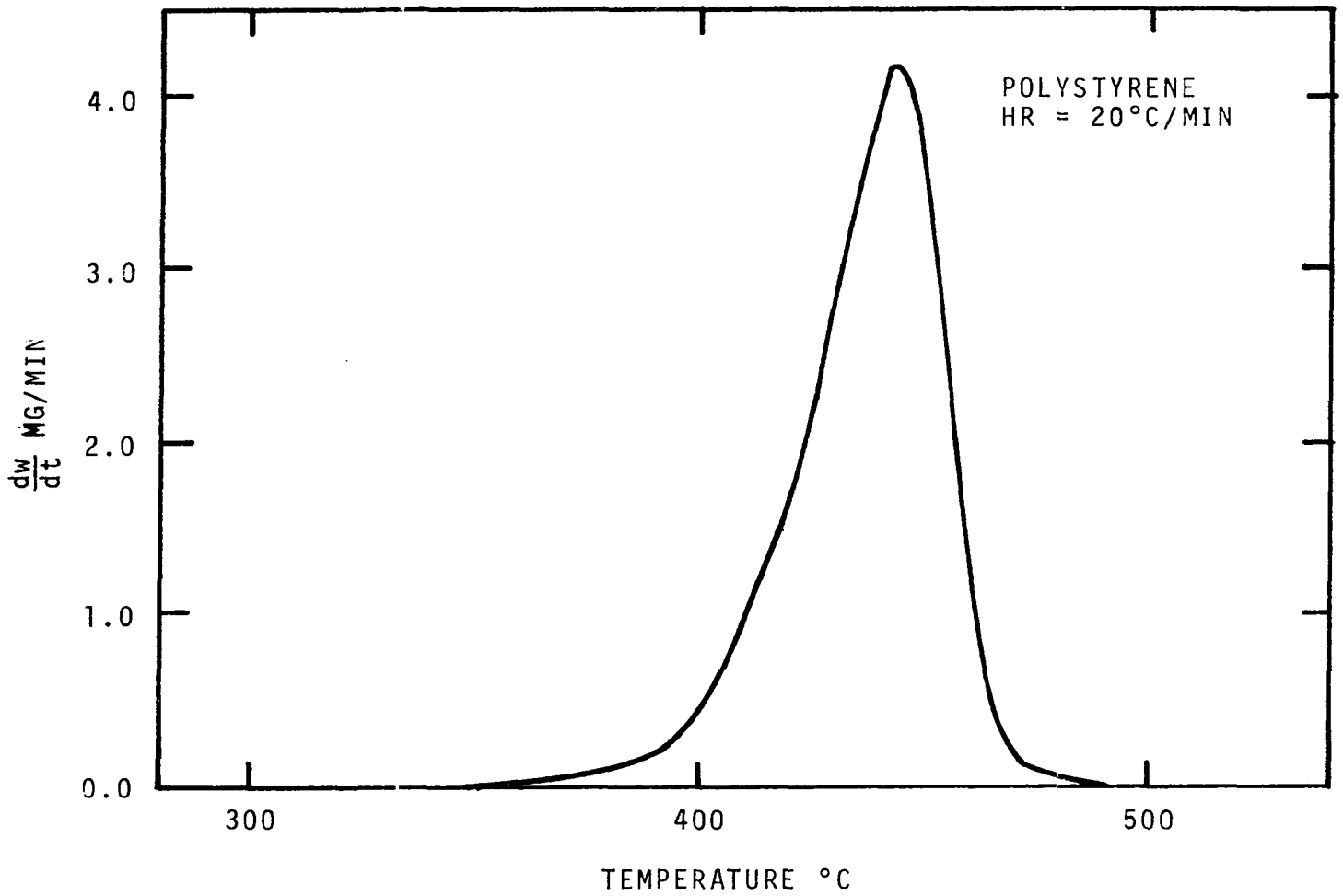

Figure II-5. Rate of Weight Loss of Polystyrene.

rates using only one set of kinetic parameters. However, the range of products obtained from the thermal degradation of polystyrene, along with the results of other methods of kinetic analysis, indicate that quite probably more than one weight loss mechanism is operative. The parameters obtained using the preceding analysis do have one big advantage in that they apply over the complete decomposition range and normally allow the weight loss kinetics to be modeled quite adequately.

Possibly the most widely used method for the kinetic analysis of dynamic thermogravimetric data is that of Freeman and Carrol (12, 13). If Equation II-10 is applied at some point, say T_1, on the experimental TGA curves,

$$\log \left(-\frac{dW}{dt}\right)_{T_1} = \log A_1 - E_1/2.3RT_1 + n_1 \log W_1 \qquad \text{(II-15)}$$

At T_2

$$\log \left(-\frac{dW}{dt}\right)_{T_2} = \log A_2 - E_2/2.3RT_2 + n_2 \log W_2 \qquad \text{(II-16)}$$

Subtracting Equation II-16 from Equation II-15 gives

$$\log \left[\left(-\frac{dW}{dt}\right)_{T_1} / \left(-\frac{dW}{dt}\right)_{T_2}\right] = \log (A_1/A_2) - E_1/2.3RT_1 + E_2/2.3RT_2 + n_1 \log W_1 - n_2 \log W_2 \qquad \text{(II-17)}$$

It is now assumed in the interval $(T_1 - T_2)$ A, E, and n may all be considered constant, or

$$\log \left[-\left(\frac{dW}{dt}\right)_{T_1} / -\left(\frac{dW}{dt}\right)_{T_2}\right] = n \log (W_1/W_2) - (E/2.3R) \cdot (1/T_1 - 1/T_2) \qquad \text{(II-18)}$$

A plot of log $[(dW/dt)_{T_1}/(dW/dt)_{T_2}]$ versus log (W_1/W_2) will enable the calculation of n from the slope of the line and E from the intercept. Normally, small, equally spaced values of $\Delta(1/T)$ are chosen, and a plot of this type is made covering the complete decomposition range. Figure II-6 is an example of the application of this technique to the polystyrene decomposition data shown in Figure II-5. Even with the smooth polystyrene decomposition curve, this method shows n and E to be changing depending on the conversion range examined. In reality, the method of Freeman and Carrol involves the same type of assumptions as the previous methods covered and yields, in general, no better or no different information.

Flynn and Wall (28) applied the method of Freeman and Carrol to two sets of calculated TGA data. The first set was calculated using the equation

$$\frac{dc}{dt} = Ae^{-E/RT} f(c) \qquad \text{(II-19)}$$

where

$$f(c) = -\frac{24}{31}\left[c^3 + c^2 - \frac{7}{4}c - \frac{1}{4}\right] \qquad \text{(II-20)}$$

E was fixed at 60,000 cal/mole and A at 10^{16}. The degradation simulated by Equations II-19 and II-20 was said to be one type of random degradation. The weight loss curve and rate of weight loss curve calculated from these equations are shown in Figure II-7. The data calculated from these equations were then plotted according to Equation II-18, and three conversion ranges were observed. The following results were

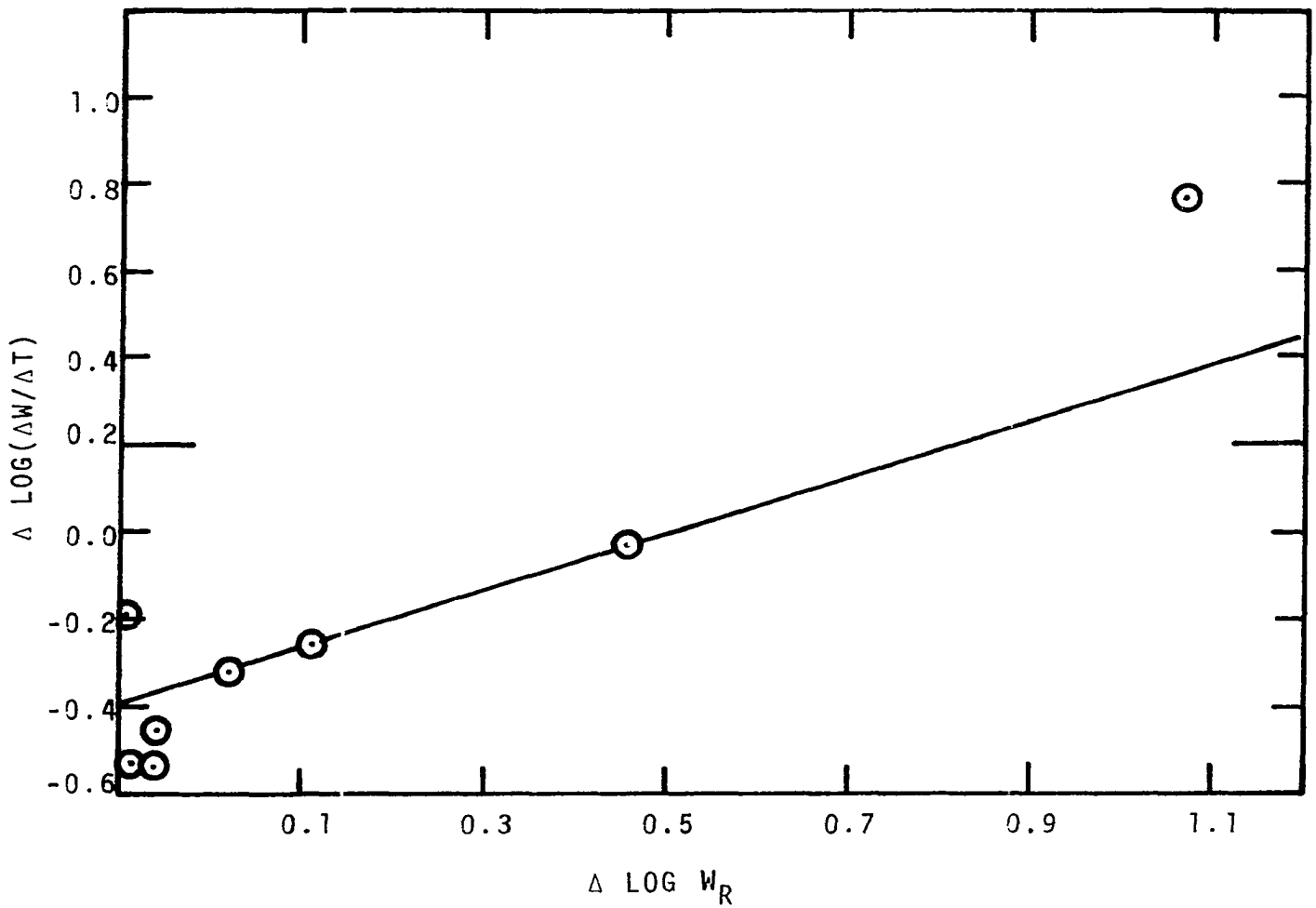

Figure II-6. Method of Freeman and Carroll (13) as Applied to the Decomposition of Polystyrene.

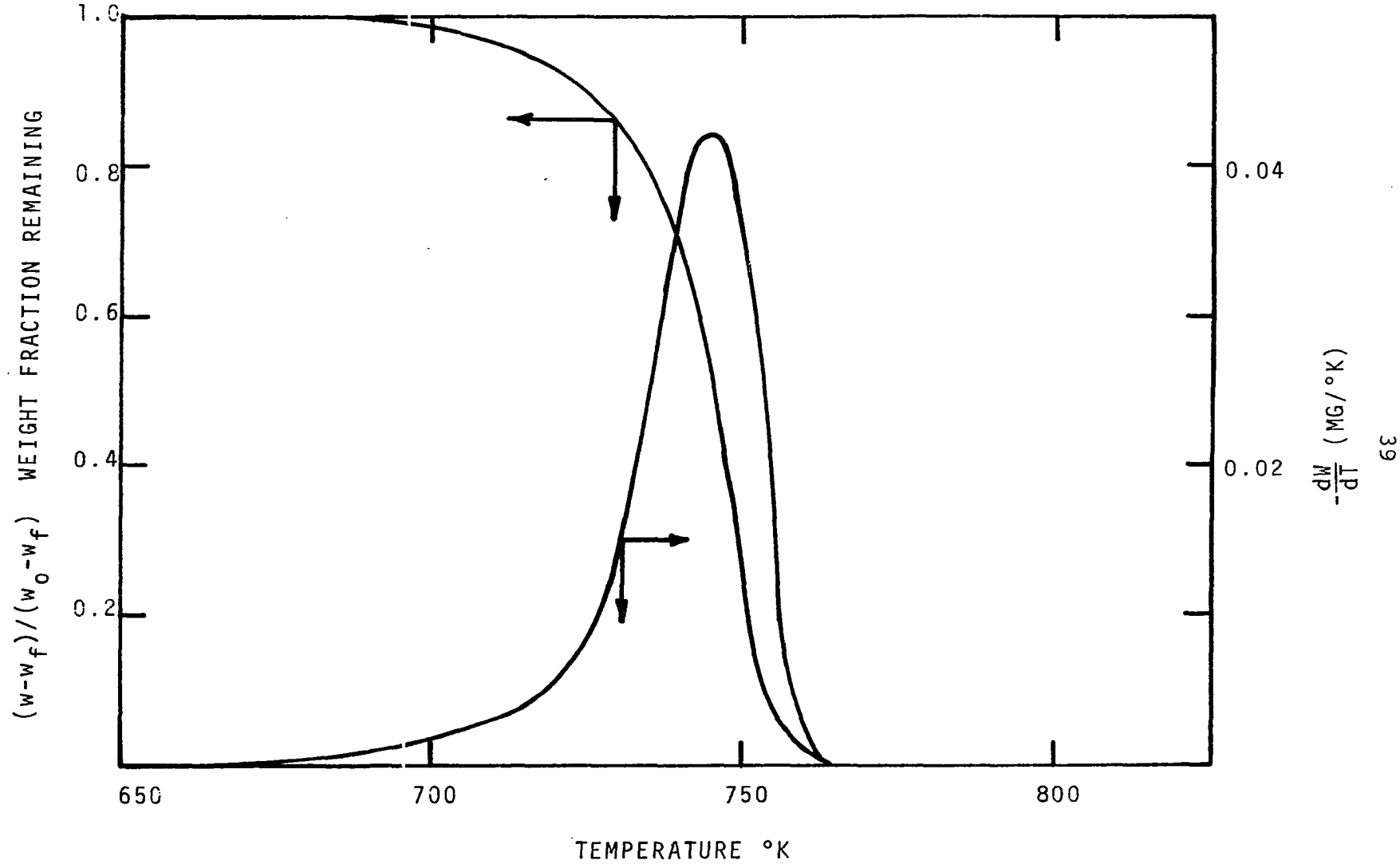

Figure II-7. Theoretical Decomposition Curves Calculated from Equations II-19 and II-20.

obtained for E and n:

1-13 percent conversion: E = 66,500 cal/mole, n = -2.4

13-50 percent conversion: E = 105,000 cal/mole, n = 0.3

50-95 percent conversion: E = 175,000 cal/mole, n = 1.25

The activation energy calculated using this technique does not correspond to the actual value used to calculated the decomposition curve except in the low conversion range. Flynn and Wall concluded for this type of kinetics the method of Freeman and Carrol may give a procedural n and E, but these have no mechanistic significance.

This technique was also applied to the theoretical case of two competitive first order reactions, represented by the following equation

$$-\frac{dW}{dt} = 4.85 \times 10^{7} e^{-30,000/RT}(W) + 10^{6} e^{-60,000/RT}(W) \quad \text{(II-21)}$$

The calculated curves for this reaction are shown in Figure II-8. When these data are analyzed according to Equation II-18 the following results are obtained. As W approaches 1 (low conversion) the curve approached the correct intercept, E = 30,000 cal/mole. However, the slight effect of the higher activation energy reaction, along with the lack of sensitivity to n in the low conversion range, causes the reaction to appear to be of zero order as W approaches 1. As W approaches 0 the slope approaches n = 1, but with an intercept of 40,000.

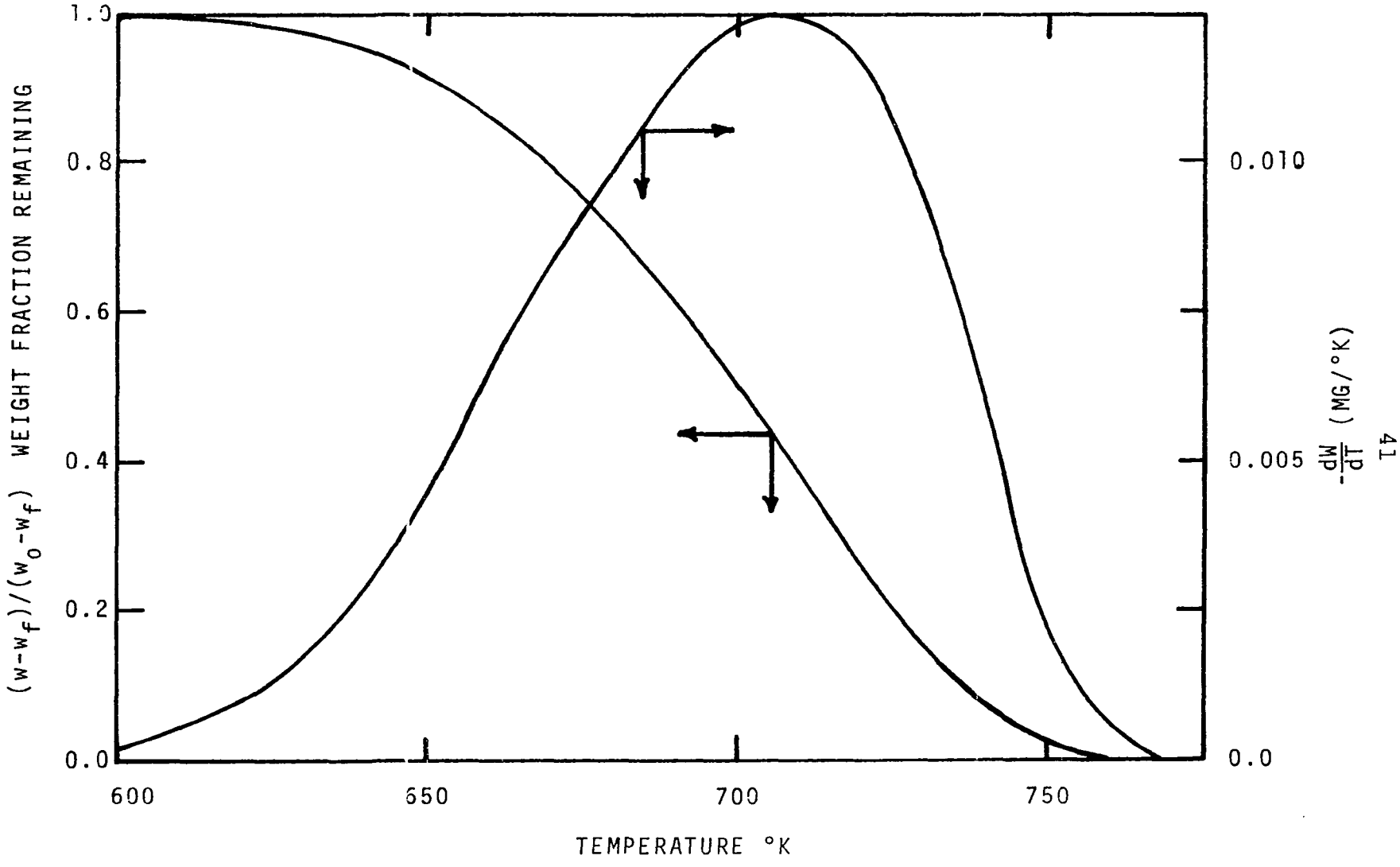

Figure II-8. Theoretical Weight Loss and Rate of Weight Loss Curves for the Case of Two Competitive Reactions, Equation II-18.

The final treatment of TGA data to be discussed was developed by Friedman (29). Reviewers (28, 30) of kinetic data analysis methods have agreed that this method is the most generally applicable treatment of TGA data available. This technique requires TGA data at several heating rates and utilizes the logarithmic form of Equation II-10

$$\log \left[-\frac{1}{w_o - w_f}\frac{dw}{dt}\right] = \log A + \log f(W) - E/2.3RT \quad \text{(II-22)}$$

The rate, $[-1/(w_o - w_f)] \cdot dw/dt$, and temperature corresponding to any particular value of f(W) are dependent on the heating rate employed. One of the major assumptions of this technique as stated by Goldfarb, is that the chemistry of the process is independent of temperature. Or, in other words, f(W) will be constant at any weight loss, $(w-w_f)/(w_o - w_f)$, regardless of heating rate. Using this assumption and plotting, at a constant value of conversion, the logarithm of the rate versus 1/T for several different heating rates, an activation energy may be obtained from the slope of the line. If this procedure is repeated for various values of conversion, a spectrum of activation energies may be obtained over the entire conversion range. An illustration of this technique using polystyrene data taken in this work is given in Figure II-9. The variation in E over the complete range of conversion may give an indication of kinetic changes that are occurring during the degradation. In some cases it may be difficult to distinguish

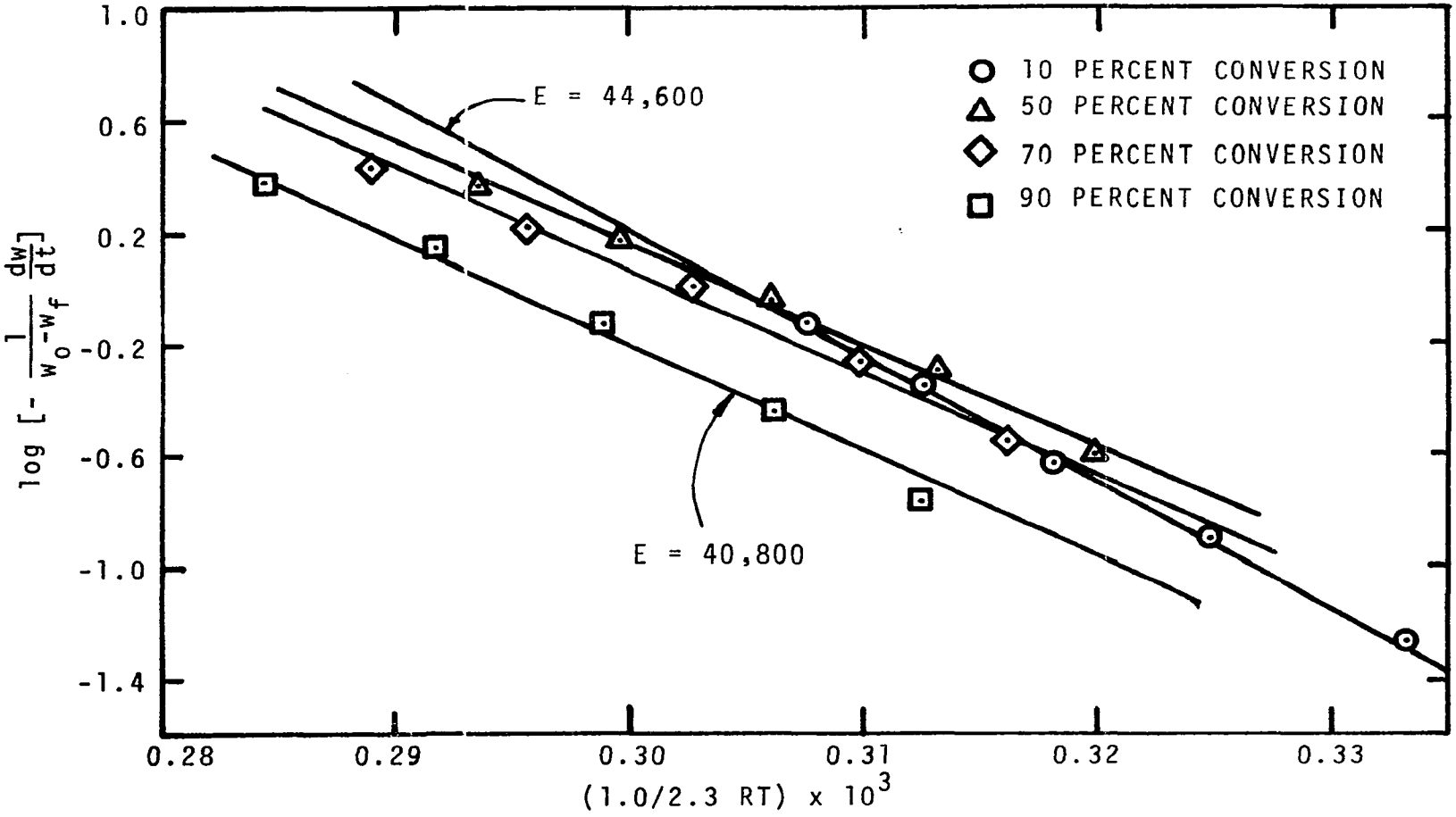

Figure II-9. Plot to Obtain Activation Energies Using the Method of Friedman, Equation II-22. Polystyrene Decomposition.

between real changes in kinetics and apparent changes due to experimental error.

The validity of the first assumption may be tested, to some extent, by examining the plotted lines used to obtain activation energies. If these lines are straight there is some confidence that the kinetics are independent of temperature. If these lines curve this assumption is quite probably a poor one. Here again, however, real changes in kinetics may be difficult to distinguish from experimental error. Also, relatively large variations in heating rates are needed to test this assumption adequately.

If the activation energies calculated do not vary much over the entire conversion range, an average activation energy may be calculated. Using this average E to determine a constant slope, it is possible to calculate from the intercepts using Equation II-22, a value of log Af(W) at each conversion. Plotting these values of log Af(W) versus W will, in many instances, enable the determination of the rate law. If this plot is a straight line, n'th order kinetics are indicated and the slope of the line gives n. If this plot is curved, the reaction may be of changing order, i.e., some type of random kinetics.

Wall and Flynn (28) modeled three different types of polymer degradation processes and applied Friedman's method. The first two reaction types were discussed previously in

dealing with the technique of Freeman and Carrol. The third case is a decomposition consisting of two independent first order reactions. This reaction is modeled by the use of

$$-\frac{1}{w_{o,1} - w_{F,1}}\frac{dw_1}{dt} = 4.458 \times 10^7 \, e^{-30,000/RT} \cdot \left(\frac{w_1 - w_{F,1}}{w_{o,1} - w_{F,1}}\right) \qquad \text{(II-23)}$$

and

$$-\frac{1}{w_{o,2} - w_{F,2}}\frac{dw_2}{dt} = 10^{16} \, e^{-60,000/RT} \left(\frac{w_2 - w_{F,2}}{w_{o,2} - w_{F,2}}\right) \qquad \text{(II-24)}$$

where $w_1 + w_2 = w$ total sample weight

$w_{o,1} + w_{o,2} = w_o$ total initial weight

$w_{F,1} + w_{F,2} = w_F$ total final weight

The decomposition curves for this degradation process at three heating rates are shown in Figure II-10 and Figure II-11.

When Equation II-22 is applied to the first reaction, a type of random degradation, a series of parallel straight lines is obtained for degrees of conversion from 0.04 to 0.95. The average value of E obtained is 59,800 ± 1500 compared with 60,000 cal/mole from which the data were originally calculated. A plot of log Af(W) versus W gives a curved line indicating some type of random degradation kinetics.

The third reaction type, that of two independent first order reactions, is also successfully analyzed using this method. In applying the technique to this reaction, it is found that at low conversions, up to approximately 0.10,

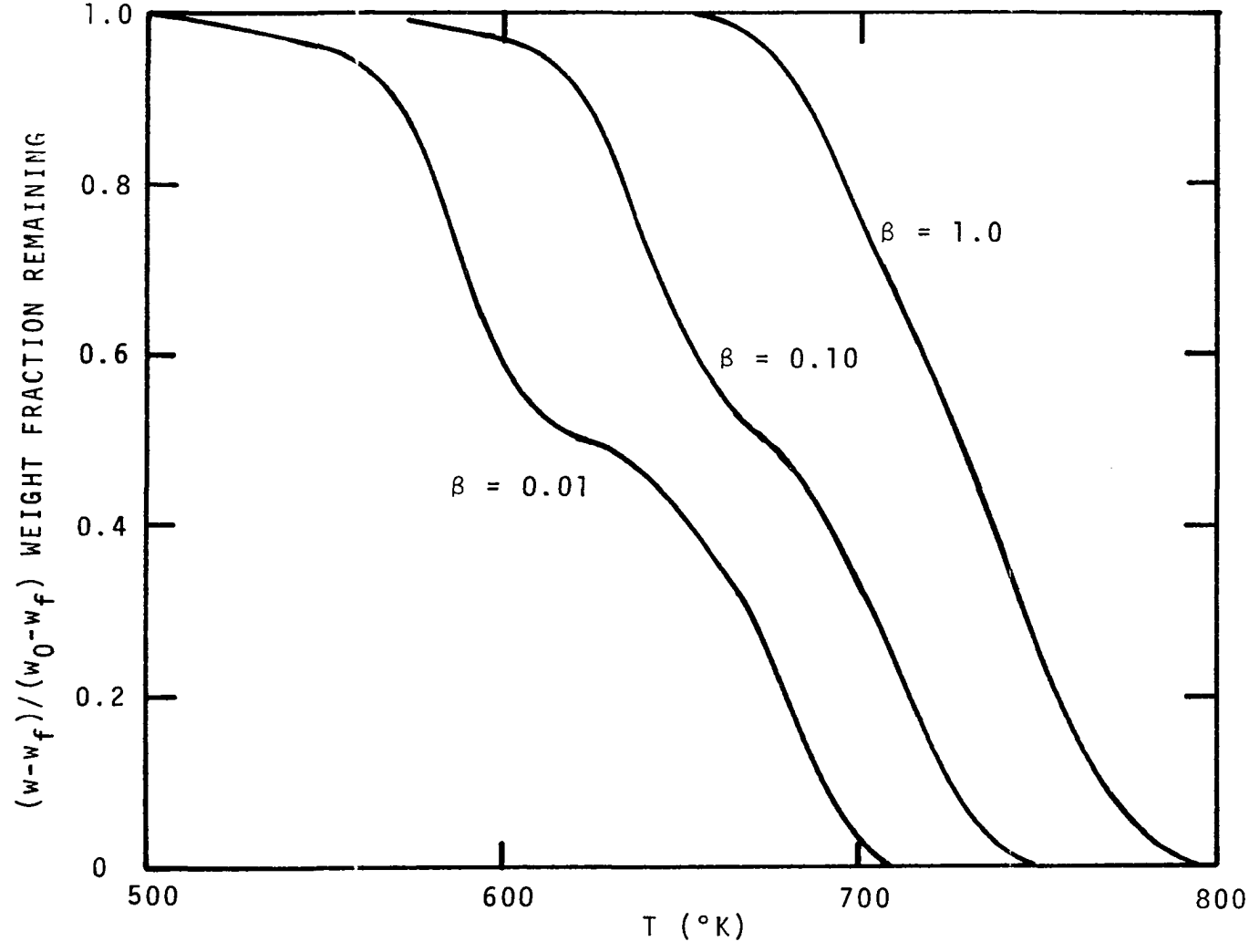

Figure II-10. Theoretical Weight Loss Curves for Two Independent First Order Reactions. β = Heating Rate.

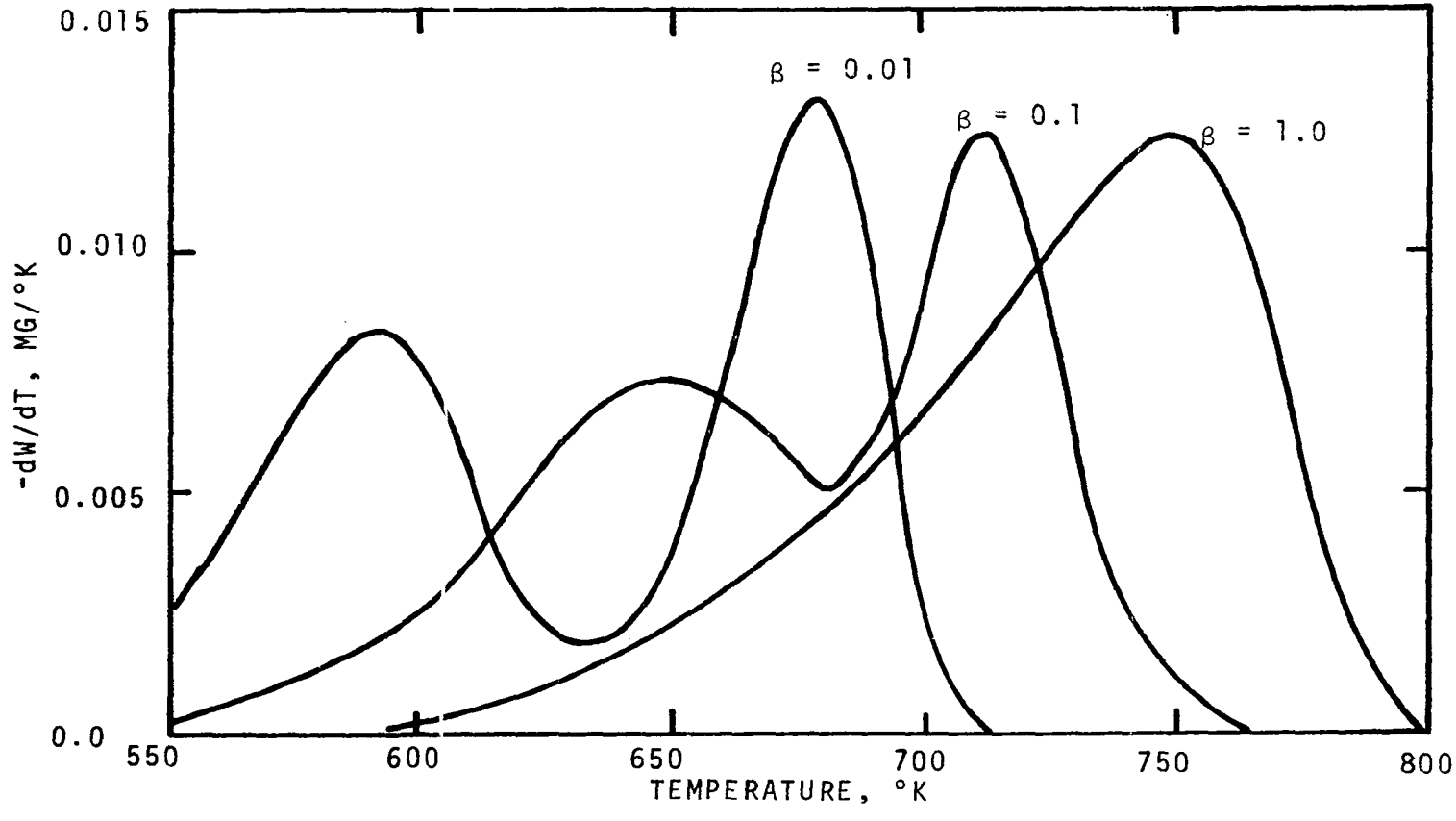

Figure II-11. Theoretical Rate of Weight Loss Curves for Two Independent First Order Reactions. β = Heating Rate.

an activation energy of 30,000 cal/mole is indicated. At high conversions, above 0.75, an activation energy of 60,000 cal/mole is obtained. As might be expected, in the intermediate conversion range values of activation energy increasing from 30,000 to 60,000 cal/mole are found as conversion increases.

In the low conversion range of the second reaction type, two competitive first order reactions, activation energies of 30,000 cal/mole are again obtained. As the reaction progresses, however, the lines plotted to obtain activation energy begin to show some curvature indicating that for this particular type of reaction the assumption of kinetics independent of temperature may not hold.

In summary, the method of kinetic data analysis developed by Friedman is the only differential technique available that allows a satisfactory analysis to be made. As was shown, even this technique was not completely satisfactory in all cases. As will be seen later, other complications arise when applying this technique to experimental data that do not occur, or are overlooked, when studying idealized data of known kinetics.

CHAPTER III

DISCUSSION OF EXPERIMENTAL STUDIES AND RESULTS

In studying the kinetics of thermal degradation of synthetic polymers there is a great need for data at high heating rates. Brown (2) stated that at heating rates up to 10°C/min the pyrolysis mechanism for polymeric materials is usually independent of heating rate. The minimum surface heating rate required for ignition is normally much higher than this, and heating rates may exist in real fires of several thousand degrees per minute. There are no data in the literature on the decomposition of synthetic polymers at heating rates in excess of 20°C/min. One of the objectives of the experimental portion of this study was to obtain kinetic data at heating rates that approach those required for ignition.

Materials Studied

Three synthetic polymers--polystyrene, polymethylmethacrylate (PMMA), and polyvinyl chloride (PVC)--were chosen for this study. Several factors influenced the selection of these polymers. The most severe constraint placed on the selection of materials to be studied was imposed by the

differential scanning calorimeter (DSC). The upper temperature limit on the DSC, before calibration, is 500°C. Since one of the major objectives of this study was to investigate the energy changes associated with thermal degradation, materials were needed that decomposed below 500°C at the heating rates under consideration. Polystyrene and PMMA both satisfied this requirement. Prior to this investigation, the Flame Dynamics Laboratory at the University of Oklahoma conducted an extensive study on the ignition characteristics of certain plastics (32). Polystyrene, PMMA, and PVC were three of the materials studied in this investigation. (It has been thought that a future study might incorporate the findings of the independent investigations on these materials.) Polystyrene, PMMA, and PVC also exhibit three different types of degradation kinetics. Another concern, therefore, was to determine to what extent the kinetics of these three different processes may be analyzed.

The thermal decomposition of two polystyrene samples, two PVC samples, and one PMMA sample was studied. One polystyrene sample was a white, high-impact polystyrene manufactured by Dow Chemical Company. The second sample was a clear polystyrene with the trade name Styrolux, manufactured by Westlake Plastics. The first PVC sample was a clear PVC manufactured by Union Carbide. The second PVC sample was an unstabilized PVC in the form of a white powder. The PMMA was clear and carried the trade name Plexiglas. It was manufactured

by Rohm and Haas. With the exception of the second PVC sample all materials were obtained in the form of thin sheets. The only preparation done on the polymers before decomposing was to grind them into small pieces in a Wiley mill. Only particles passing through a 40 mesh screen were used for analysis.

Equipment and Experimental Technique

The weight loss characteristics of the polymers under consideration were studied using a Perkin-Elmer TGS-1 Thermobalance and UU-1 Temperature Control Unit. A photograph of this equipment is shown in Figure III-1. A Texas Instrument Servowriter-II was used to record the output from the thermobalance. The weighing mechanism in the TGS-1 is a Cahn-RG Electrobalance. This balance is capable of detecting weight changes of 10^{-6} grams. Suspended from the arm of the balance is a "hang-down" wire approximately 7 in long. The sample pan is held in a stirrup on the lower end of the hang-down wire. The furnace used to heat the sample surrounds the sample pan and extends approximately 1/2 in above the level of the pan. A schematic drawing of this arrangement is shown in Figure III-2. The hang-down wire serves two extremely useful purposes, both of which stem from isolating the decomposing sample from the electrobalance. First, the furnace is far enough removed from the electrobalance that the heat from the furnace does not affect the weighing mechanism.

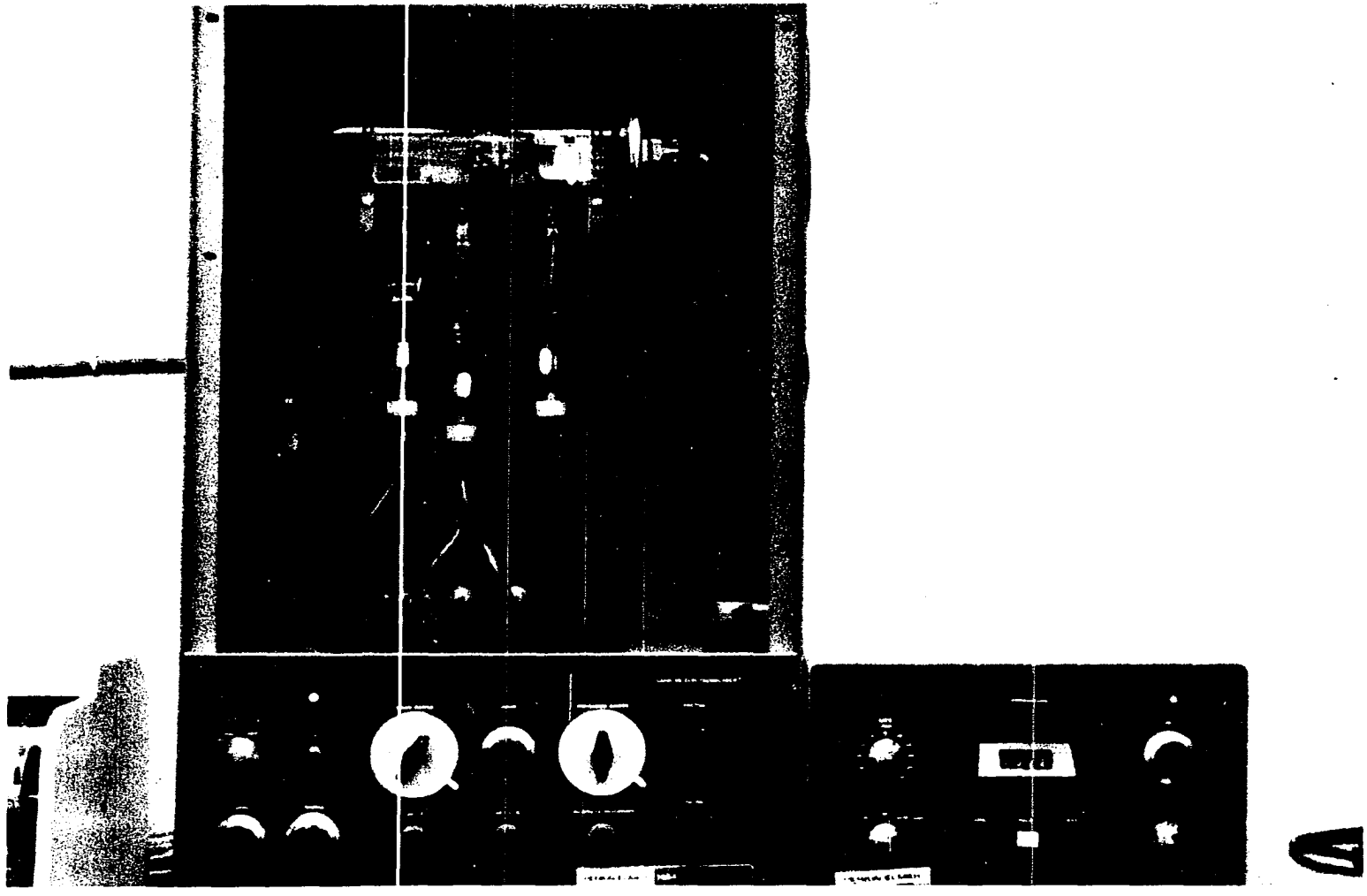

Figure III-1. Perkin-Elmer TGS-1 Thermobalance and UU-1 Temperature Controller.

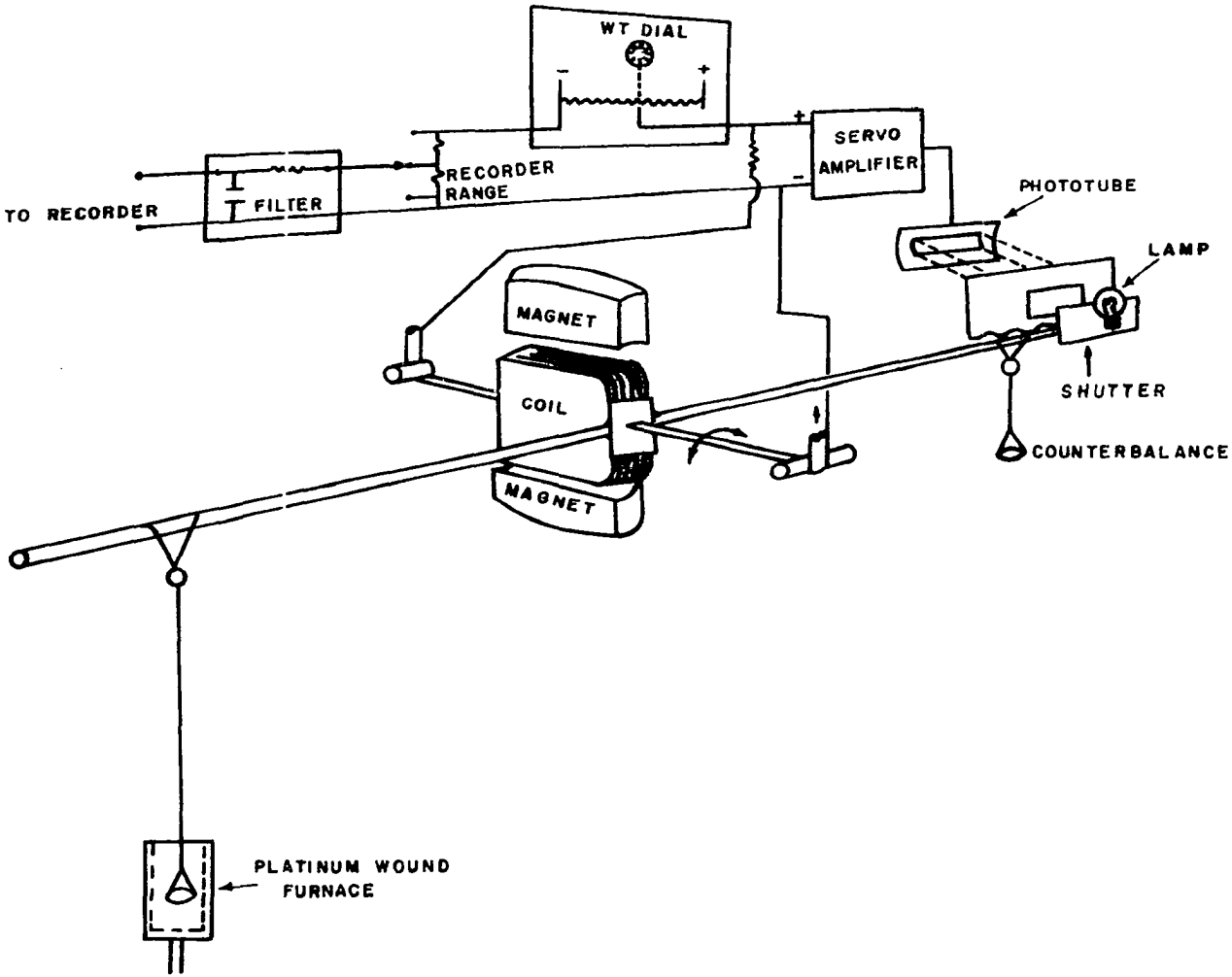

Figure III-2. Schematic of Perkin-Elmer TGS-1 Furnace and Weigh Assembly.

Second, the isolation of the sample from the electrobalance permits the decomposition products to be swept away by a purge gas before they have an opportunity to condense on the balance and possibly foul the delicate components.

The furnace used in conjunction with the TGS-1 consists of a small ceramic cylinder wound with platinum wire. The platinum wiring is covered with a thin film of insulation. A ceramic collar is fitted over the furnace and the bottom of the collar plugged with quartz wool which protects the wiring from the decomposition products. The early furnaces used with the TGS-1 did not have this collar for protection, and they would normally fail after only a few sample runs. If, after each sample run, the furnace is allowed to stand in air at 800°C to oxidize all traces of residue, the furnaces will withstand up to 150 heating cycles before failing.

A Perkin-Elmer UU-1 Temperature Control Unit is used to control the temperature and the heating rate of the furnace. The heating rate is adjustable in multiples of two from 0.3125 to 160°C/min. The temperature may be programmed upward or downward and stopped manually or automatically at any temperature between ambient and 1000°C. The UU-1 may also be set to cool automatically at 320°C/min upon reaching a preset temperature. A small indicator light is mounted on the front of the TGS-1 control panel that is lighted when the UU-1 is in control of the furnace temperature.

The TGS-1 thermobalance requires calibration for both weight and temperature. A wide range of weight adjustments is available on the TGS-1 depending on the maximum weight change expected during the sample decomposition. On the 1 mg setting a 1 mg weight change will cause the recorded pen to be deflected full scale (250 mm). On the 2 mg setting a 1 mg weight change will cause the pen to deflect 125 mm, and so forth. The weight calibration was carried out on the 1 mg setting which involved adjusting the TGS-1 so that a 1 mg weight change caused a pen deflection of exactly 250 mm. This calibration was checked at least once each day during the course of the experimental investigation.

Perkin-Elmer has developed a unique method of temperature calibration for the TGS-1 thermobalance. This technique involves the use of several ferromagnetic alloys. Small samples, 1-2 mg, of several of these alloys are placed in the sample pan. A magnet is then placed on the outside of the furnace around the sample hangdown tube. The magnetic field causes the metal alloys to exert a downward force on the sample pan. As the temperature of the furnace is programmed upward the alloys lose their magnetic properties at known, repeatable temperatures which causes a sudden apparent weight change on the thermobalance. The temperature at which an individual alloy loses its magnetic properties is called the magnetic transition temperature. A list of the alloys available for temperature calibration and their magnetic transition

temperatures are given in Table III-1. By comparing the digital temperature readout on the UU-1 Temperature Control Unit with the known transition temperatures, the TGS-1 may be adjusted to give a linear temperature increase and calibrated for temperature. In this study an individual calibration was done at each heating rate investigated and checked several times during the use of that heating rate. A typical temperature calibration curve is shown in Figure III-3. The results of three separate checks on this one calibration are shown to give an idea of the reproducibility of the calibration.

TABLE III-1

MAGNETIC STANDARDS FOR TGS-1 FURNACE CALIBRATION

Metal	Magnetic Transition Temperature, °C
Monel	65
Alumel	163
Nickel	354
Numetal	393
Nicoseal	438
Perkalloy	596
Iron	780
Hi-Sat 50	1000

It can be seen from Figure III-3 that were it not for the point at 438°C, the temperature calibration would be very nearly linear. Using the curve shown to correct the temperatures on experimental weight loss data introduced a jog in the weight loss and rate of weight loss curves. Examination of the calibration curves obtained by previous investigators

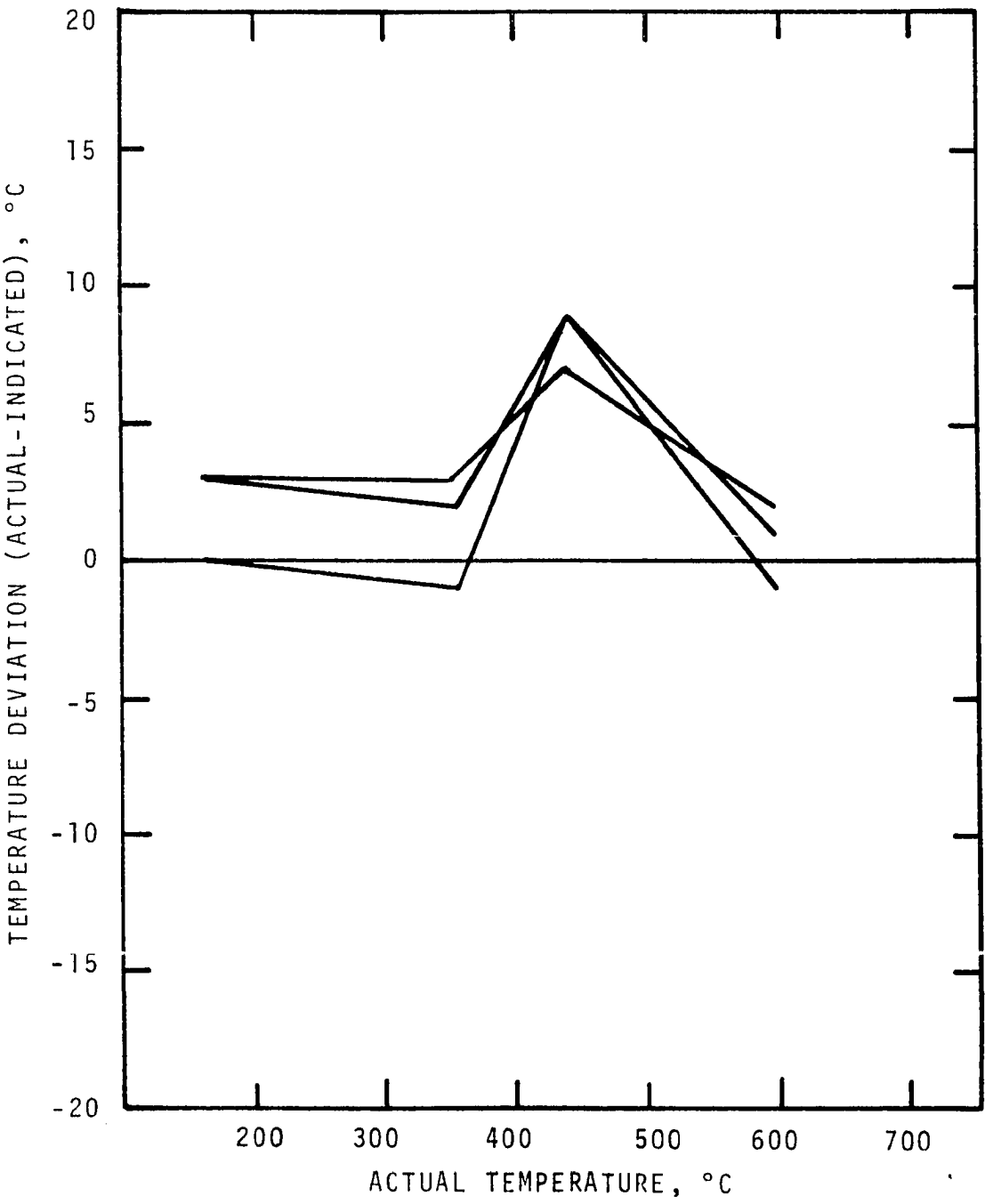

Figure III-3. TGS-1 Temperature Calibration Curve. Heating Rate 80°C/min.

revealed a similar situation. It appears that the calibration point at 438°C is in error, and for this reason the point at 438°C was ignored and the other three points used for temperature calibration. A letter was written to Perkin-Elmer asking if they had observed this situation and questioning the reported magnetic transition temperature of Nicoseal (438°C), but at this time no reply has been received.

The TGS-1 Thermobalance has the capability of internally differentiating the weight loss signal giving as the output signal the derivative of weight with respect to time. However, the TGS-1 can send only one of these signals to the recorder. This design has made it necessary in the past to make one sample run to obtain the weight loss curve and a second run, with a different sample, to obtain the rate of weight loss curve. To overcome this problem a Cahn No. 3100 Time Derivative Computer, Mark II, was purchased. This computer is connected directly to the TGS-1 enabling the weight loss and derivative weight loss to be obtained from a single experiment. This arrangement has, along with the obvious time saving advantage, the advantage of giving a direct correspondence between the two curves.

The Cahn Time Derivative Computer was essentially calibrated for each sample run. The area under the dw/dt curve given by the computer represents the total weight lost by the sample during its decomposition. For each run the weight loss can be determined independently, and by measuring

the area under the dw/dt curve the proper ordinate values may be obtained from

$$\text{ordinate (mg/sec-cm)} = \frac{\text{weight loss (mg)} \times \text{chart speed (cm/sec)}}{\text{Area (cm)}^2} \quad \text{(III-1)}$$

Energy changes occurring during decomposition were studied using the Perkin-Elmer DSC-1b Differential Scanning Calorimeter. A photograph of the calorimeter is shown in Figure III-4. An excellent discussion on calorimetry in general, and the relative merits of the DSC-1b as compared to similar instruments, has been presented by Havens (1). Only a brief and somewhat simplified description of the DSC-1b will be presented, followed by a discussion of the major problem affecting its successful operation.

The DSC-1b sample holder assembly consists of two sample holders, one for the polymer sample and one a reference, and an inlet and exit line for the purge gas. Each sample holder has its own platinum resistance heater and temperature sensing element for temperature measurement and control. The electrical circuitry of the DSC-1b is responsible for maintaining the two holders at the same temperature and measuring the difference in the amount of electrical energy supplied to the two holders while maintaining this temperature equality. The output signal generated by the DSC-1b is this difference in electrical energy.

Each sample holder has a radiation dome to help provide a constant surface for radiation heat transfer. Ideally,

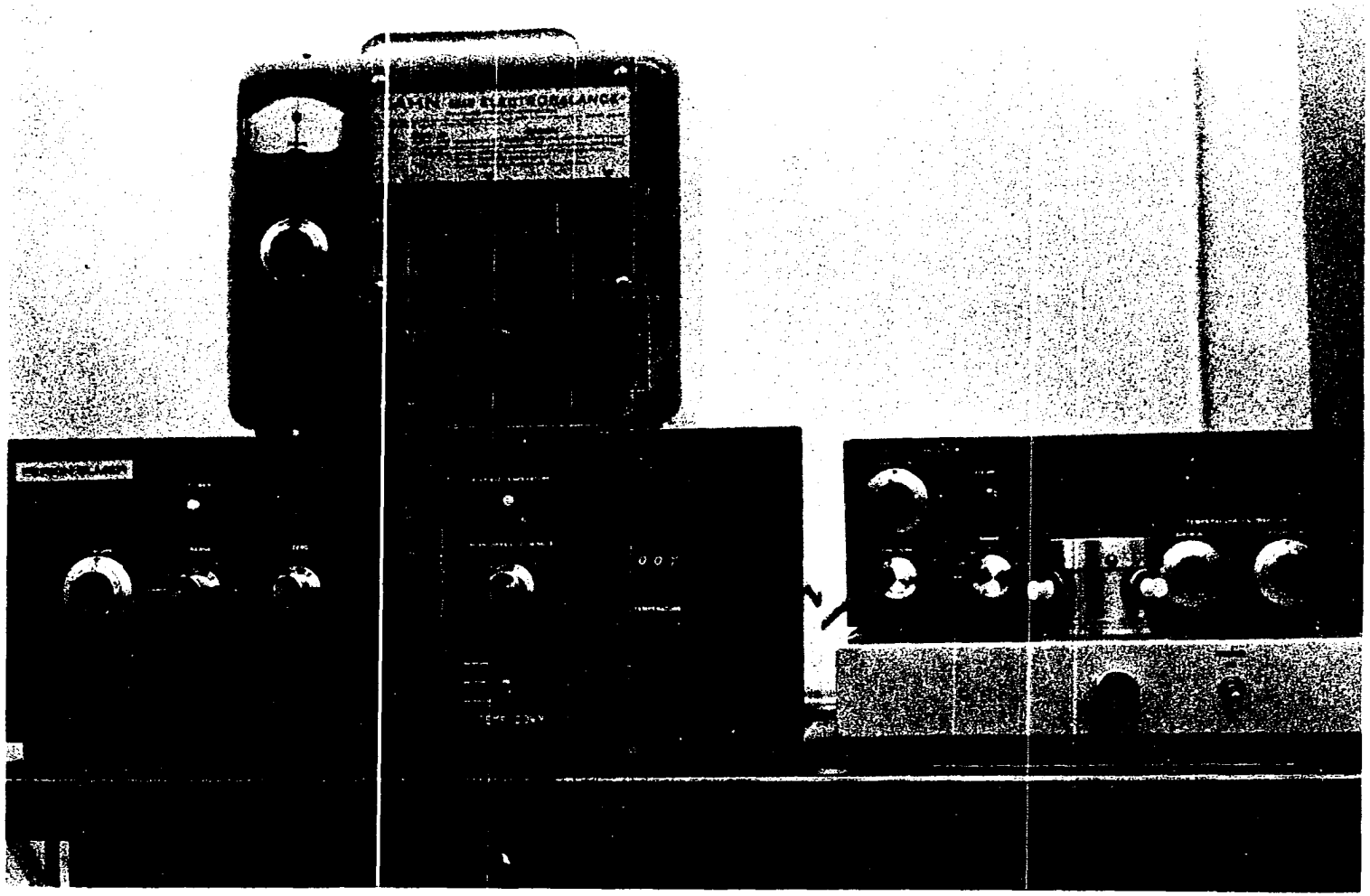

Figure III-4. Perkin-Elmer DSC-16.

if the two sample holders had exactly the same mass and heat capacity, and if the heat transfer characteristics of the two holders were identical, with both holders empty the amount of differential energy required to maintain the two holders at the same temperature would be zero. Then, if a sample were placed in one holder and the other left empty, the differential energy required would reflect only the energy requirements of the sample. Practically this is impossible to achieve. This problem is partially overcome by running a "no sample" baseline. With both sample pans empty the temperature of the DSC-1b is programmed upward exactly as it will be done during the sample run, and the differential energy requirement of the two holders is recorded as the no sample baseline. A sample is then placed in the sample pan and run under identical conditons. The no sample baseline furnishes a line of zero energy requirement relative to the sample run. The energy requirements of the sample may then be obtained by difference between the sample run and the baseline run.

The problem that remains, and it is a very significant one, is assuring that the heat transfer characteristics of the two holders are the same during the sample run and the baseline run. If these heat transfer properties change, the differential energy supplied the two holders will reflect not only the energy requirements of the sample but also the energy requirements due to the change in these properties. Fortunately the DSC-1b is capable of detecting if these heat transfer

characteristics change between the sample run and the baseline run. At the beginning and end of each sample run and each baseline run the DSC is held at an isothermal condition and allowed to come to steady state. At isothermal conditions the heat losses from the two sample holders should be the same regardless of the content of the holders. Thus, during isothermal operation at the beginning and end of the two runs, the sample line and the baseline should coincide. If the lines do not coincide there is a good indication that the heat transfer characteristics have changed. Figures III-5a and b are hypothetical examples of a successful (i.e., repeatable baselines) and an unsuccessful DSC run.

The placement of the radiation domes on the sample holders, the emissivity of the radiation domes, the flow pattern of the purge gas around the sample holders, and other factors influence the heat losses from the two holders. The two major influences are the temperature and emissivity of the radiation domes. Havens (1) has shown how a 10 percent change in the effectivity emissivity of a radiation dome could cause a change in heat losses that is over twenty times larger than the energy input due to sample heat capacity. Emissivity changes are due mainly to oxidation of the dome surface and condensation of the volatile products of decomposition on the dome surface. Proper conditioning of the radiation domes and adequate purging of the sample holder assembly will eliminate the problem of oxidation to a great extent.

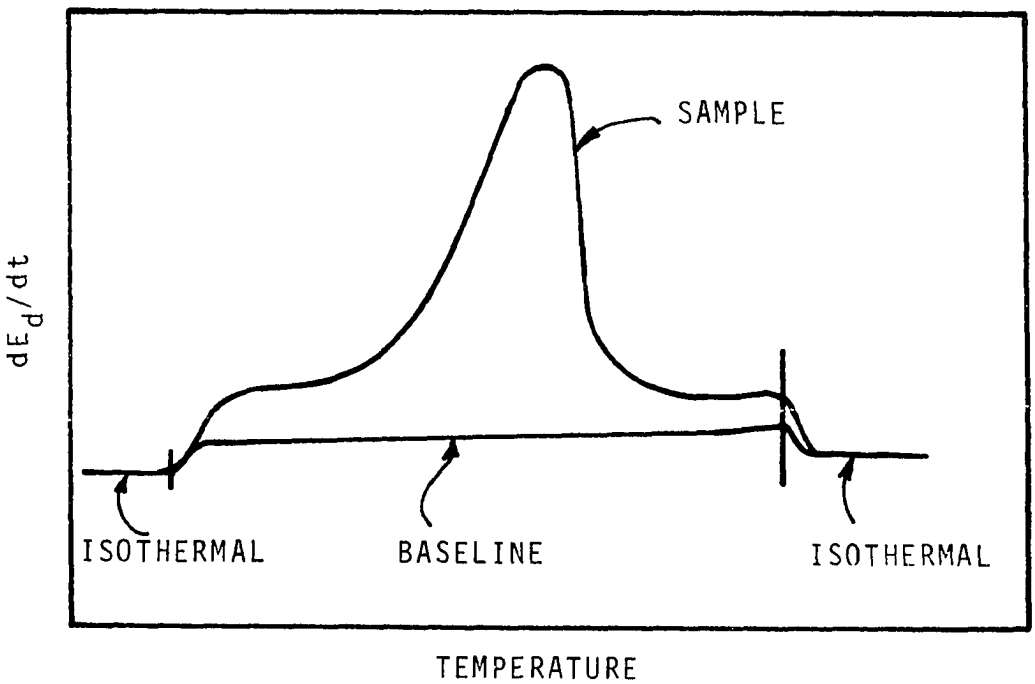

Figure III-5a. Hypothetical Successful DSC Run.

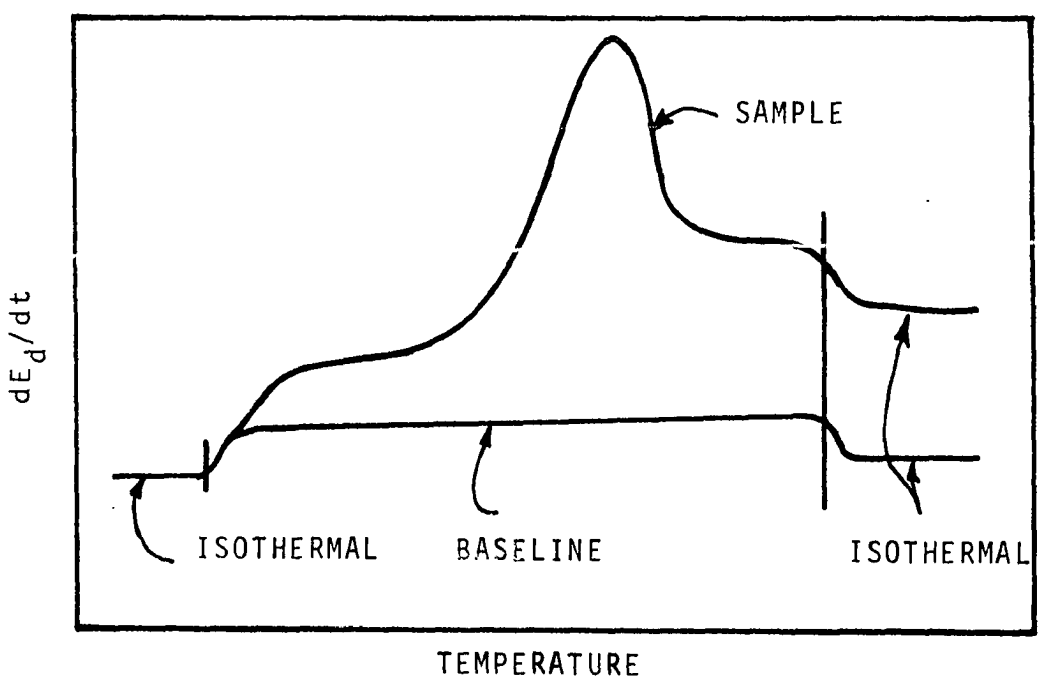

Figure III-5b. Hypothetical Unsuccessful DSC Run.

Condensation of the volatile decomposition products is much more difficult to deal with. Temperature differences of the radiation domes, occurring from run to run, may be another major source of error in DSC operation. The circuitry of the DSC-1b is designed to maintain temperature equality between the two sample holders, which is no guarantee of the temperature equality of the radiation domes. Temperature differences could result from not allowing the sample holder assembly to come completely to steady state at the beginning of each run or from volatile products contacting the sample radiation dome. It is felt that the major contributor to errors in DSC operation is the contacting of the radiation domes by the volatile products of degradation. The use of as small a sample as possible helps reduce the above mentioned problems. The nature of the decomposition products, and as a consequence the particular material under consideration influences the successful operation of the DSC to a large extent. Materials that produce a high percentage of light decomposition products are much more amenable to a successful investigation than those materials that produce heavy, easily condensable products. Providing a method for the volatile products of degradation to exit the sample holder would be a significant contribution to DSC operation procedure.

One simple change in experimental technique proved to be successful in reproducing the isothermal heat losses. Previously the baseline run was made before the sample run.

This technique required that, between the baseline and sample runs, the cover of the sample holder assembly be removed and replaced, the radiation dome on the sample holder be removed and replaced, and the sample pan taken out and replaced after filling with sample and weighing. The sample holder assembly was then purged with nitrogen which required adjustments to be made in the nitrogen flow rate. In this investigation it was found that by running the sample first and the baseline second, the isothermal heat losses were more accurately reproduced. One advantage of making the baseline run after the data run is that no part of the sample or its environment needs to be disturbed between runs.

The DSC-1b requires three separate calibrations. A differential calibration is performed to ensure that both sample holders are at the same temperature as the temperature is programmed upward. To accomplish this calibration a pure substance that undergoes a known energy transition is placed in each pan. The melting points of the pure metals indium, tin, lead, and zinc are used for this calibration. The temperature is then programmed upward at the heating rate of interest, and the DSC is adjusted until the energy transition occurs in both pans at the same temperature. This calibration is checked at the melting points of all four of the metals. A differential temperature calibration within ± 1°C is normally achieved over the range of melting temperatures, 156°-419.5°C, covered by these metals. An average temperature calibration

is then performed to correlate the actual temperature of the sample pans with the temperature of the digital indicator on the DSC. This calibration compares the known melting temperatures of the four metals with the indicated melting temperatures. A typical temperature calibration curve is shown in Figure III-6. The third calibration is performed to obtain the proper ordinate values of the curves recorded from the DSC-1b. An accurately known quantity of one of the metals is placed in one pan. The temperature is then programmed upward through the melting transition of this metal. Knowing the energy of transition for the melting process (the heat of fusion), the ordinate reading may be obtained from

$$\underset{(\text{mcal/sec-cm})}{\text{Ordinate}} = \frac{\text{Heat of Fusion } \underset{(\text{mcal/mg})}{} \times \text{Sample Wt. } \underset{(\text{mg})}{}}{\text{Area under Peak } (\text{cm}^2)} \times \underset{(\text{cm/sec})}{\text{Chart Speed}} \qquad \text{(III-2)}$$

The ordinate value obtained in this manner will depend on the DSC-1b range (sensitivity) setting. To convert from the range setting used on the calibration run to another range setting the following equation is used

$$\text{New Ordinate} = \frac{\text{New Range}}{\text{Calibration Range}} \times \text{Calibration Ordinate} \qquad \text{(III-3)}$$

The results of the ordinate calibration runs for this study are shown in Table III-2.

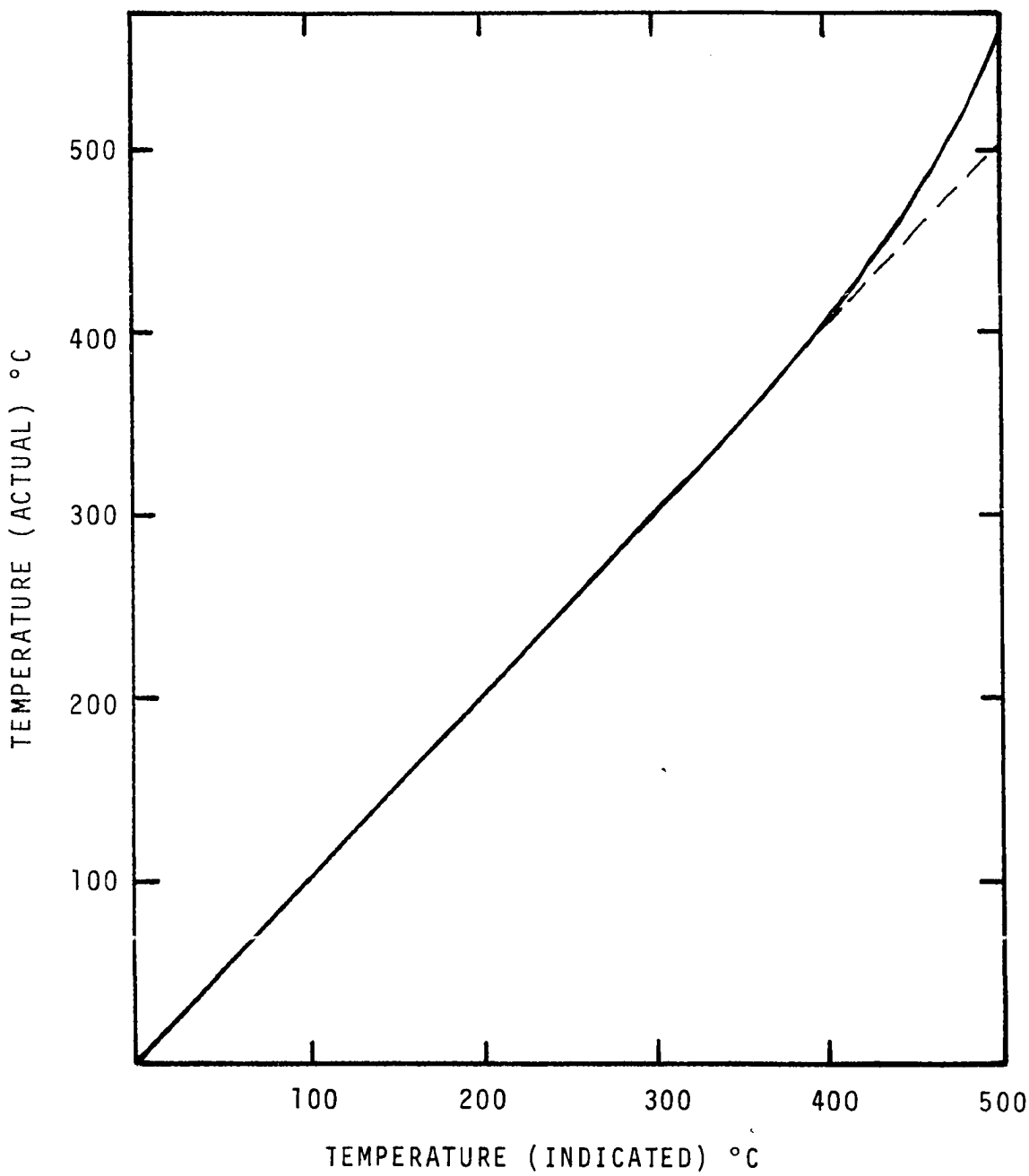

Figure III-6. DSC Temperature Calibration Curve.

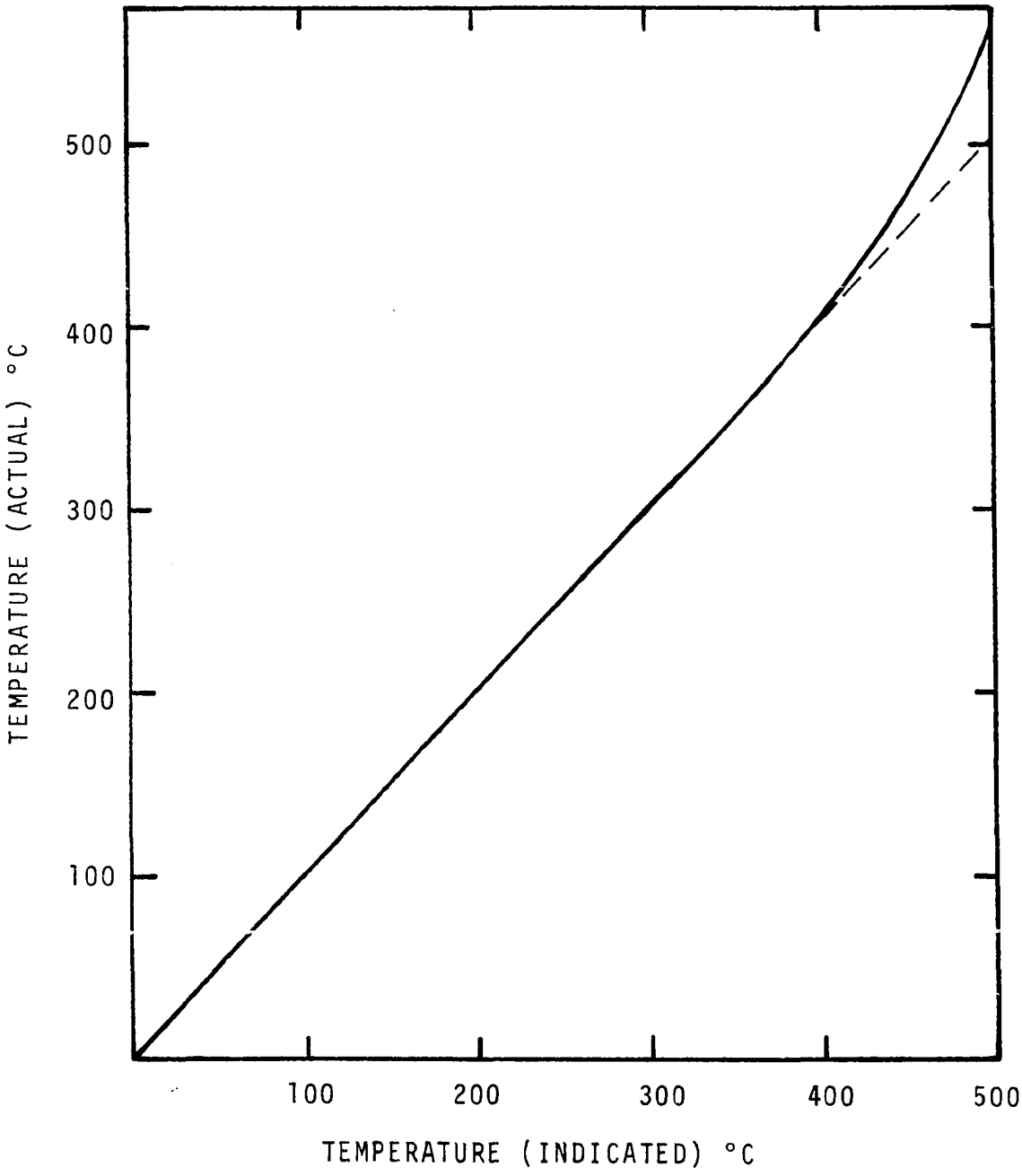

Figure III-6. DSC Temperature Calibration Curve.

TABLE III-2

DSC ORDINATE CALIBRATION RESULTS

Run No.	Sample	Sample Weight (mg)	Range	Chart Speed (in/min)	Area Under Curve (cm^2)	Ordinate (mcal/cm-sec)
1	Indium	6.27	16	4	10.61	40.5
2	Indium	6.27	16	4	10.67	40.3
3	Indium	6.27	32	4	5.35	80.5
4	Indium	6.27	32	4	5.31	81.0
5	Zinc	5.00	16	4	31.09	39.8
6	Zinc	5.00	16	4	31.96	38.8
7	Zinc	5.00	32	4	16.20	76.5
8	Zinc	5.00	32	4	14.72	84.1

Experimental Results

The weight loss kinetics of polystyrene, PMMA, and PVC were studied in a flowing nitrogen atmosphere at heating rates of 10, 20, 40, 80 and 160°C/min. A nitrogen flow rate of 40 cc/min was used. Three runs of each polymer sample were made at each heating rate for a total of seventy-five individual TGS runs. The weight loss and rate of weight loss for the five samples studied are shown in Figures III-7 through III-31. At the three higher heating rates it was observed that samples larger than approximately 4 mg showed slight heat transfer effects. Heat transfer effects, as used here, mean that the polymer sample is too large to accurately follow the programmed temperature of the TGS-1. As a consequence, the average sample temperature is below the indicated temperature, which causes a slight shift in the weight loss and rate of weight loss curves. Data were not available to make a systematic study of these heat transfer effects. All data reported in Figures III-7 through III-31 were taken with samples smaller than 4.5 mg. Pertinent data for all seventy-five TGA runs are given in Appendix A.

As the heating rate is increased the weight loss and rate of weight loss curves shift toward higher temperatures. This effect is shown for clear polystyrene in Figure III-32. A similar shift is found in the other polymers. The reason for this shift may be seen by examining the equation used to describe the weight loss kinetics

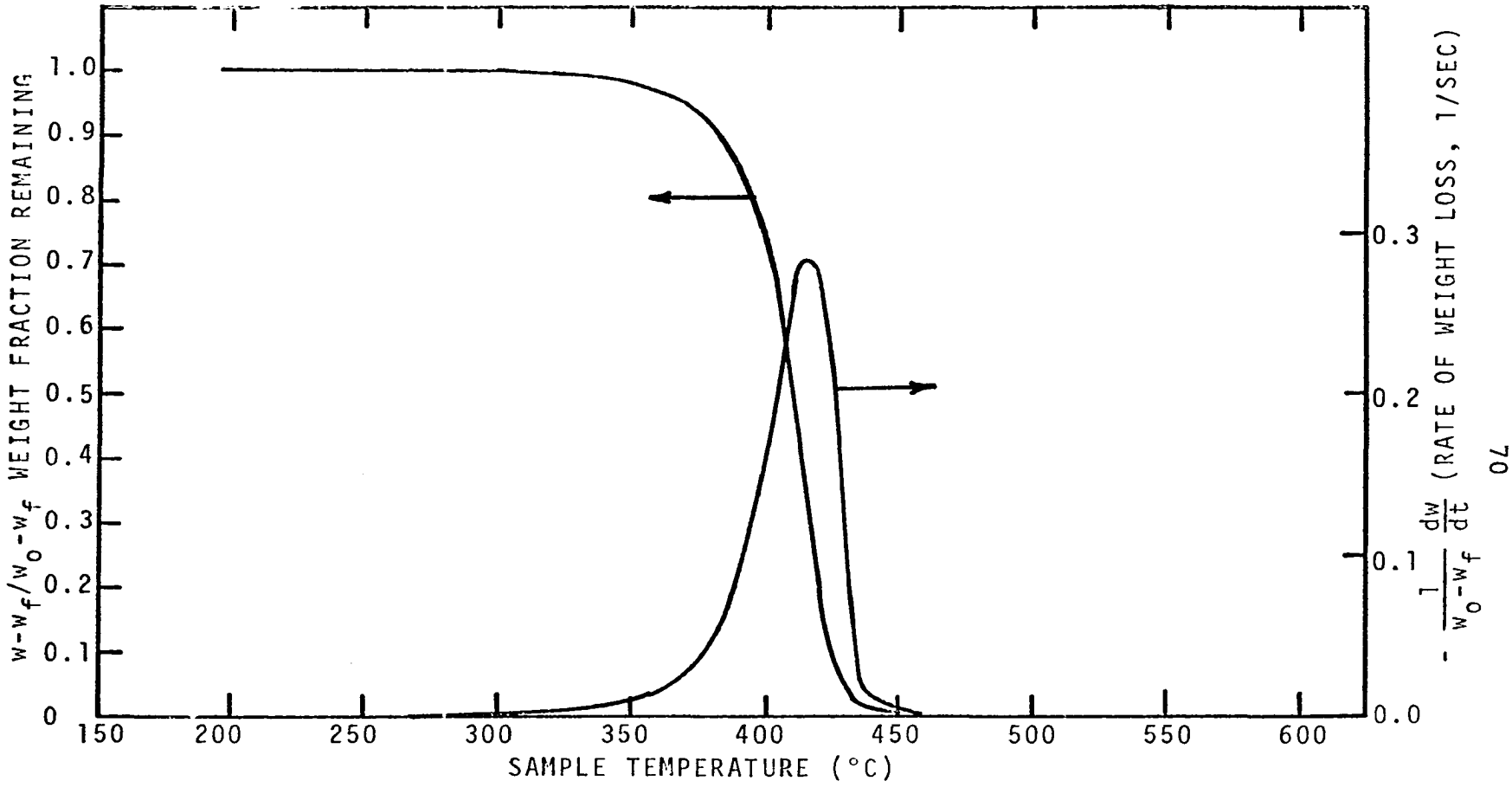

Figure III-7. Weight Loss and Rate of Weight Loss for Clear Polystyrene. Heating Rate - 10°C/min.

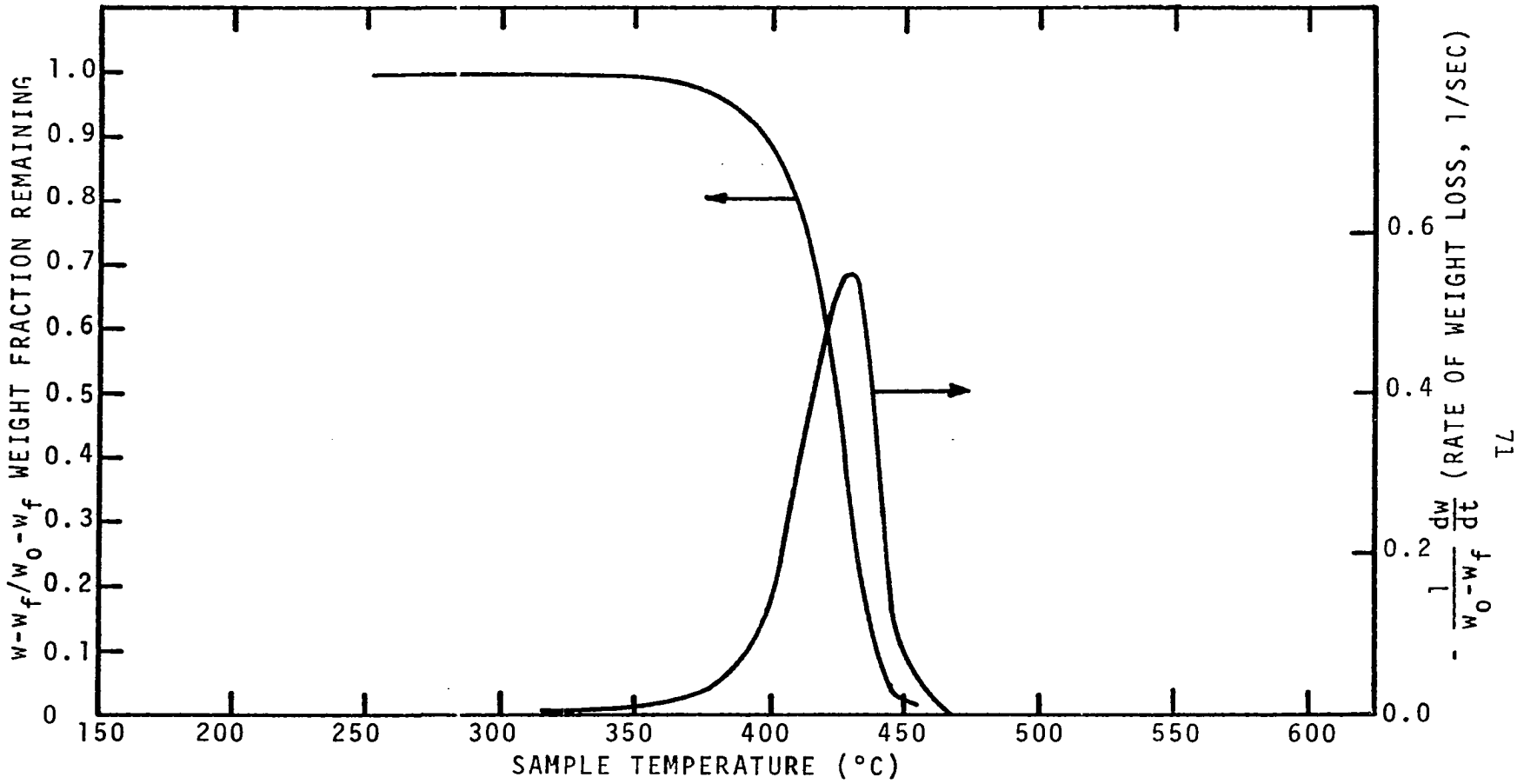

Figure III-8. Weight Loss and Rate of Weight Loss for Clear Polystyrene. Heating Rate - 20°C/min.

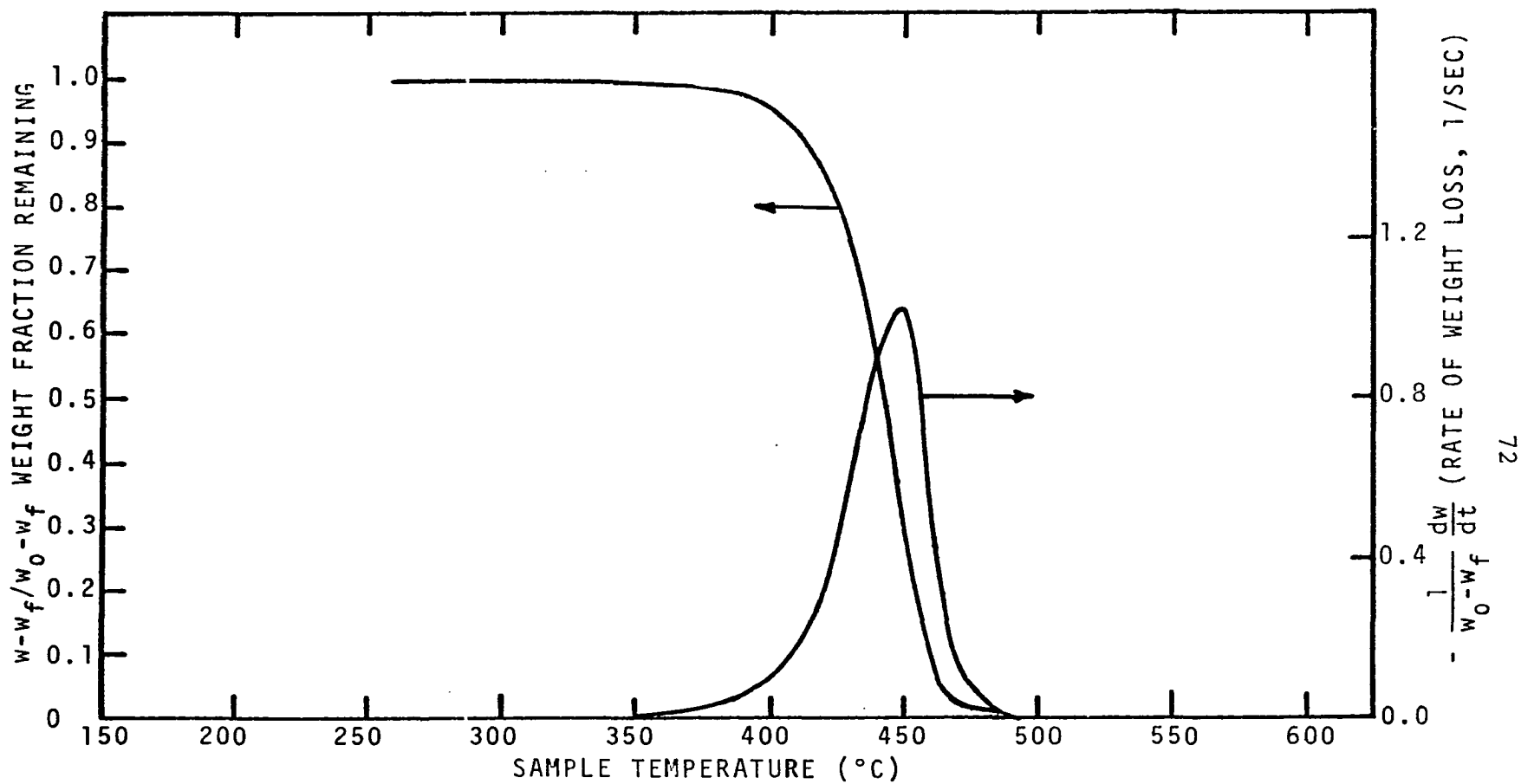

Figure III-9. Weight Loss and Rate of Weight Loss for Clear Polystyrene. Heating Rate - 40°C/min.

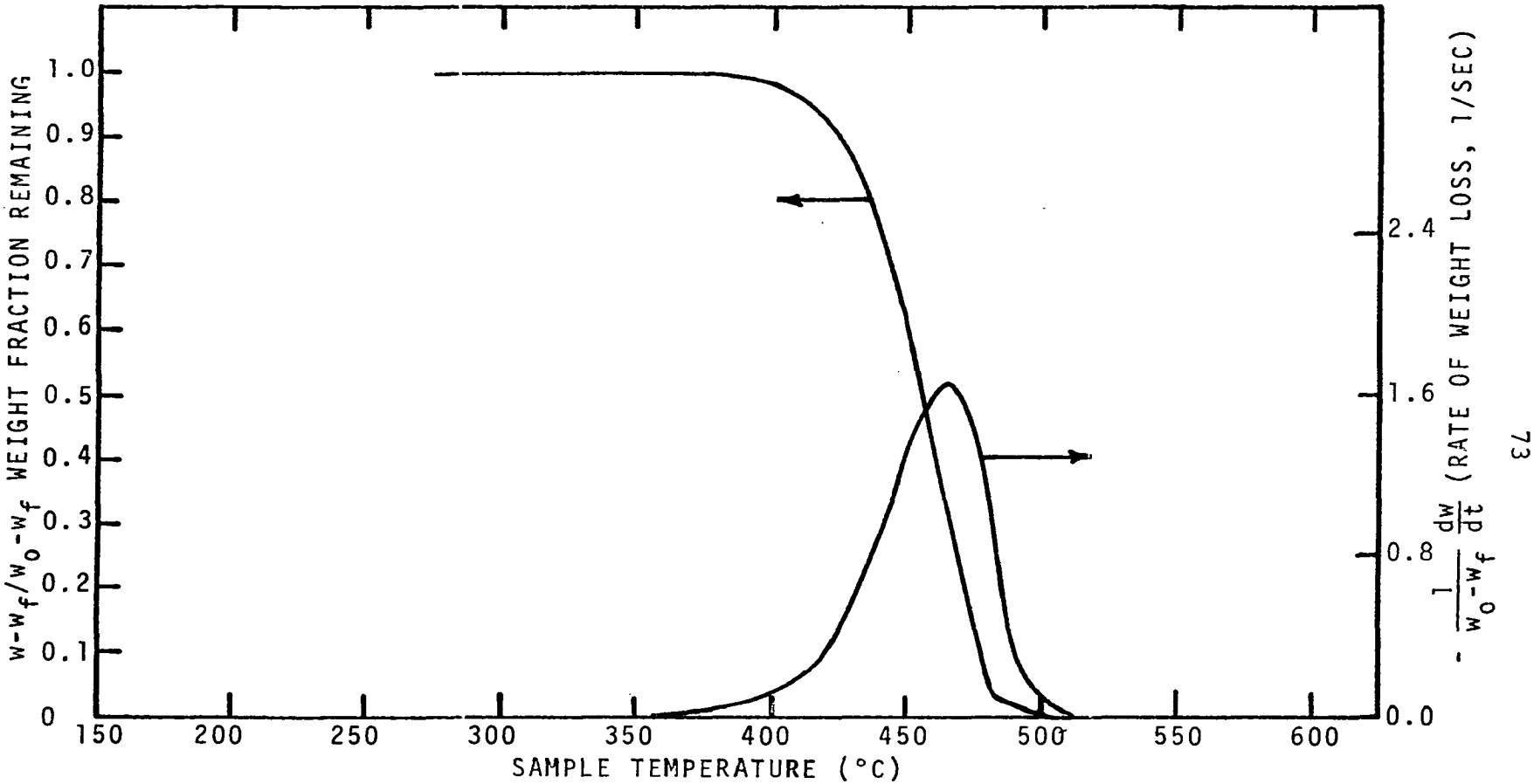

Figure III-10. Weight Loss and Rate of Weight Loss for Clear Polystyrene. Heating Rate - 80°C/min.

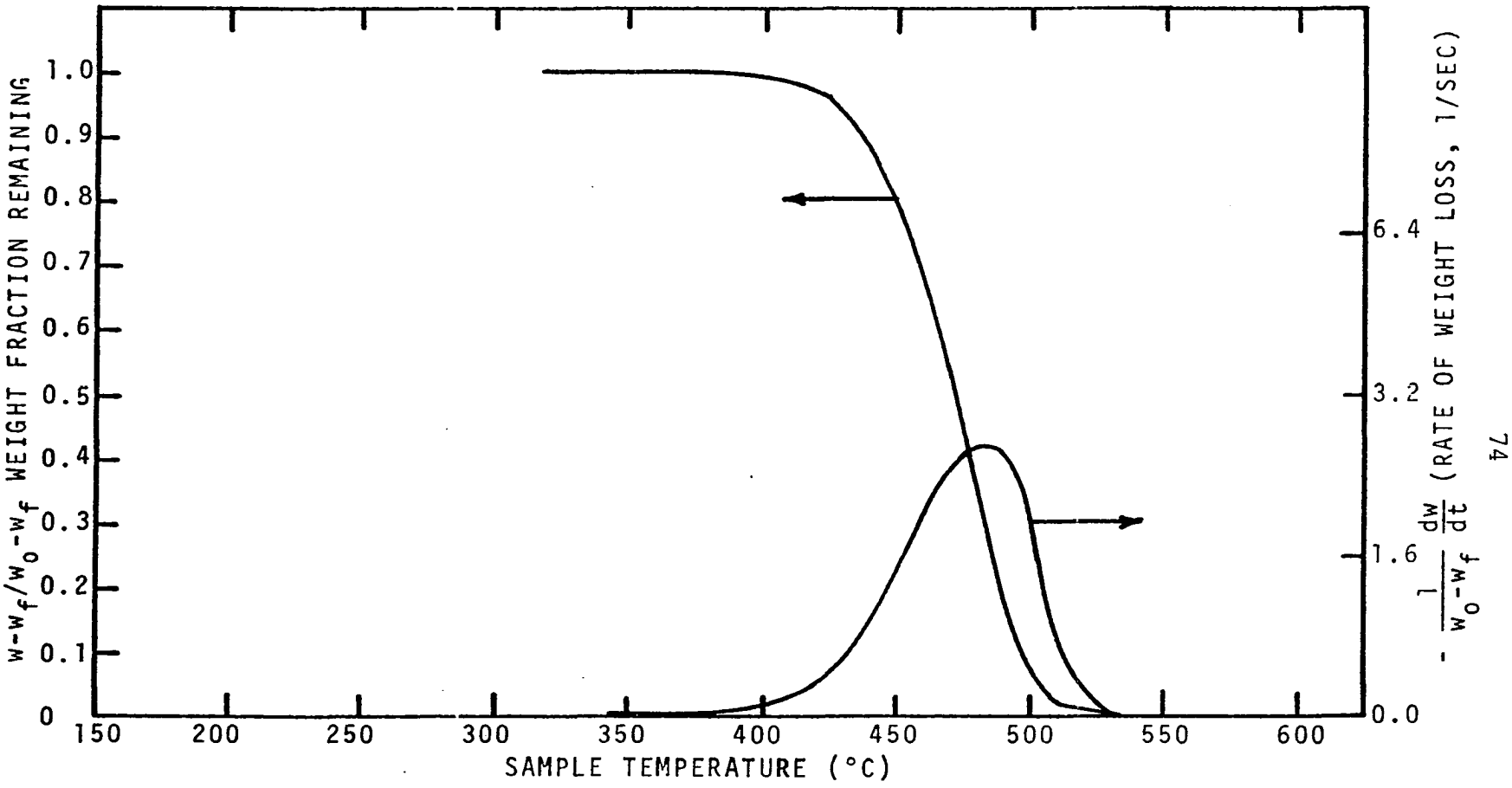

Figure III-11. Weight Loss and Rate of Weight Loss for Clear Polystyrene. Heating Rate - 160°C/min.

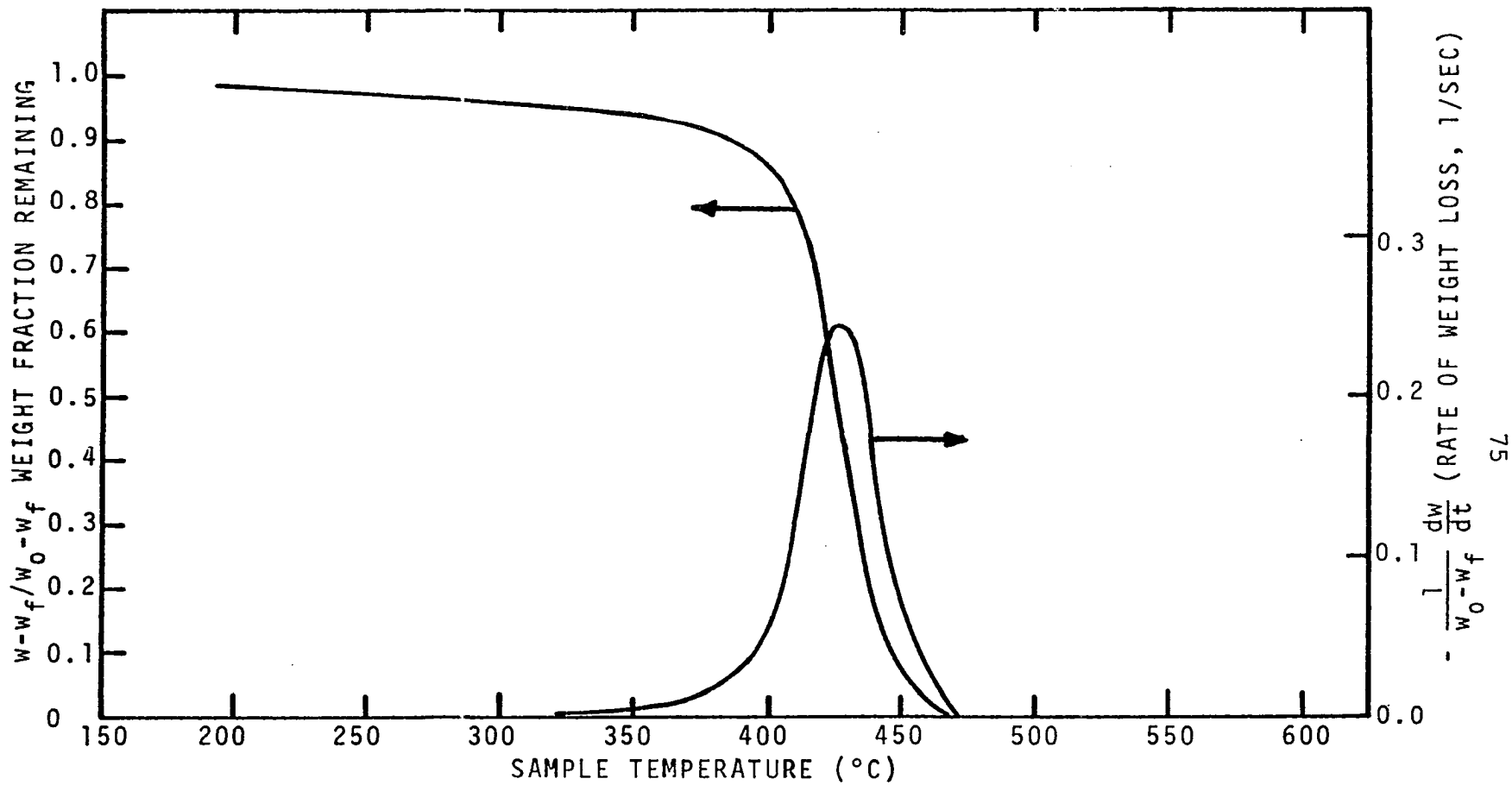

Figure III-12. Weight Loss and Rate of Weight Loss for White Polystyrene. Heating Rate - 10°C/min.

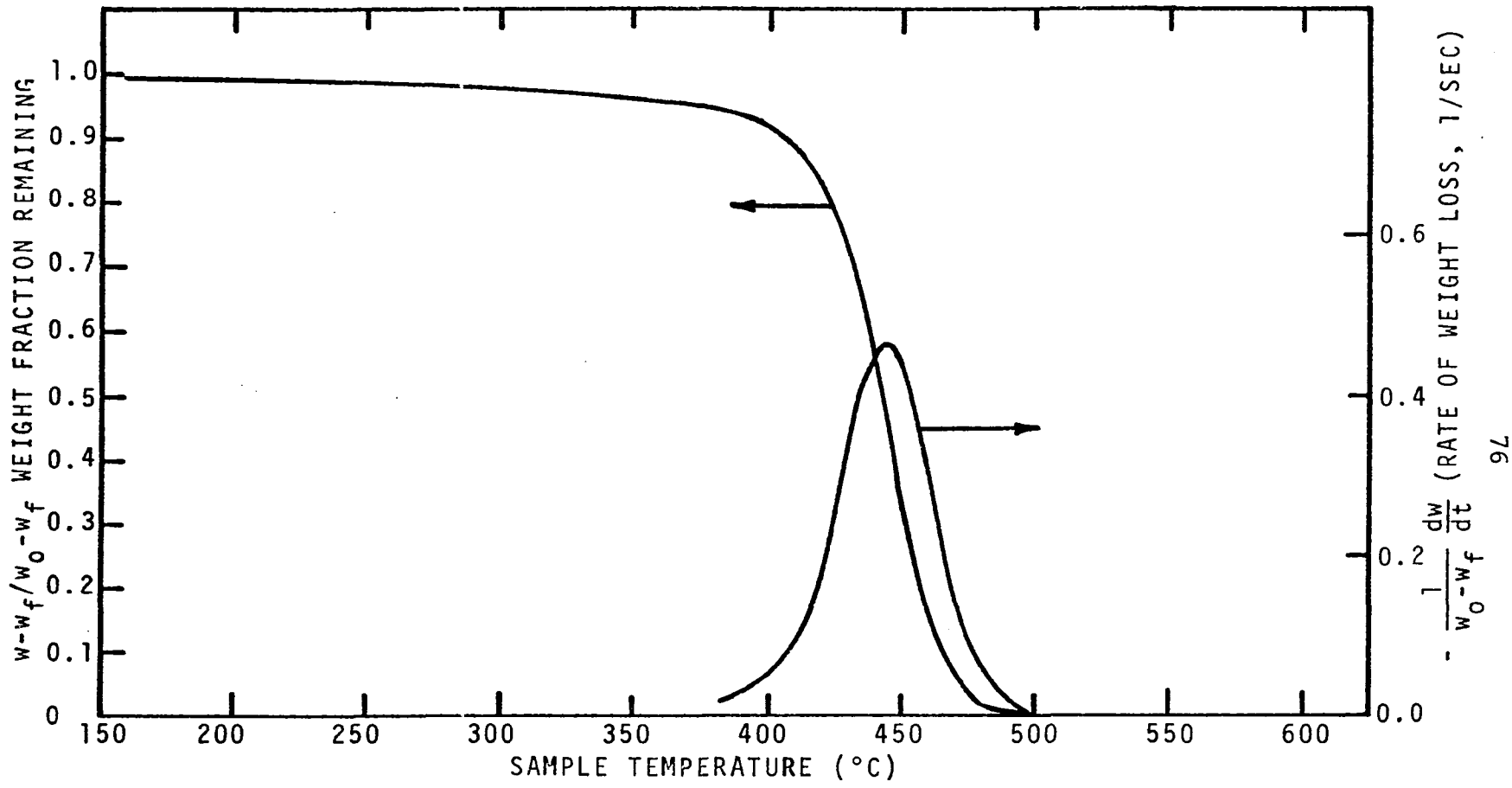

Figure III-13. Weight Loss and Rate of Weight Loss for White Polystyrene. Heating Rate - 20°C/min.

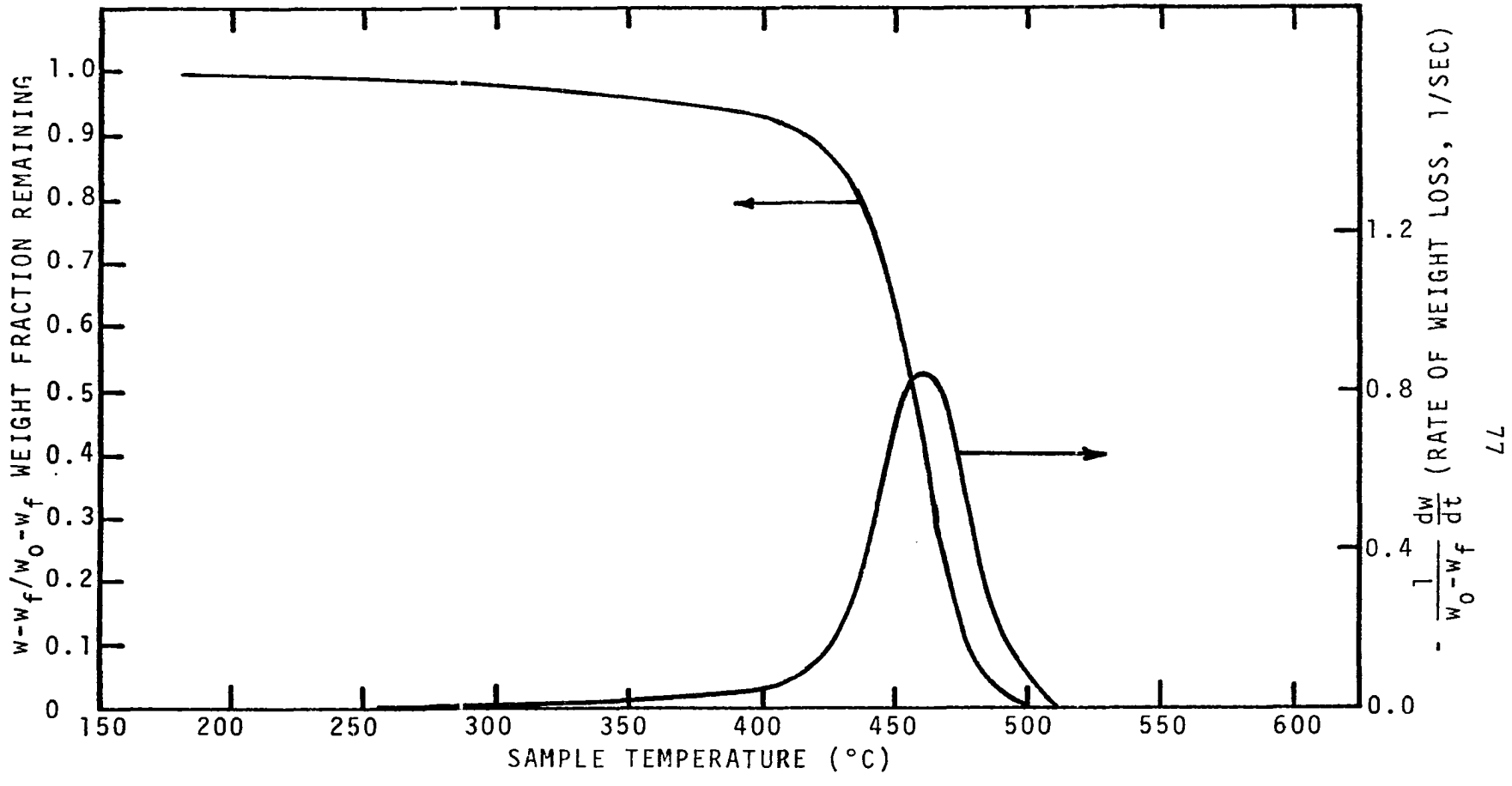

Figure III-14. Weight Loss and Rate of Weight Loss for White Polystyrene. Heating Rate - 40°C/min.

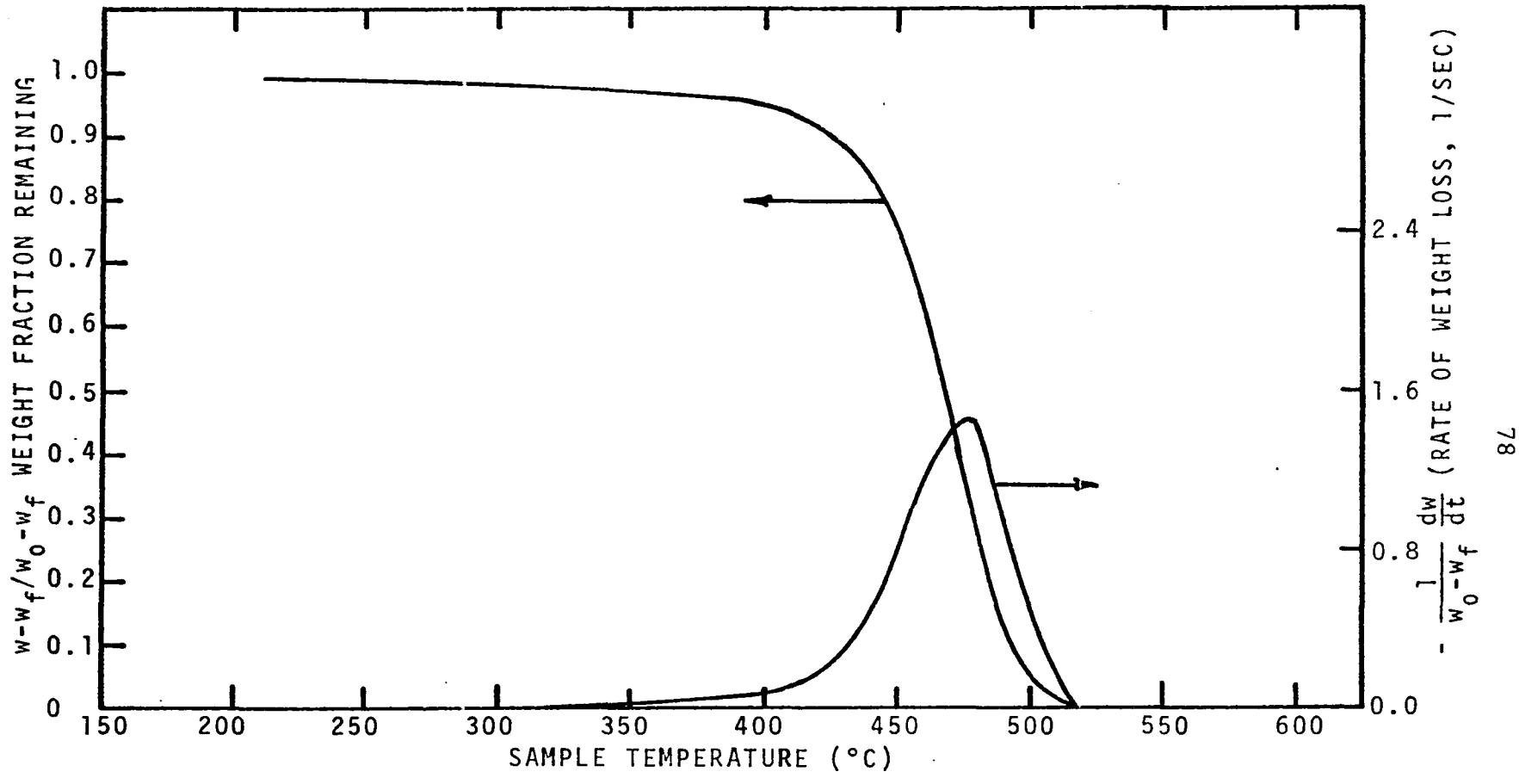

Figure III-15. Weight Loss and Rate of Weight Loss for White Polystyrene. Heating Rate - 80°C/min.

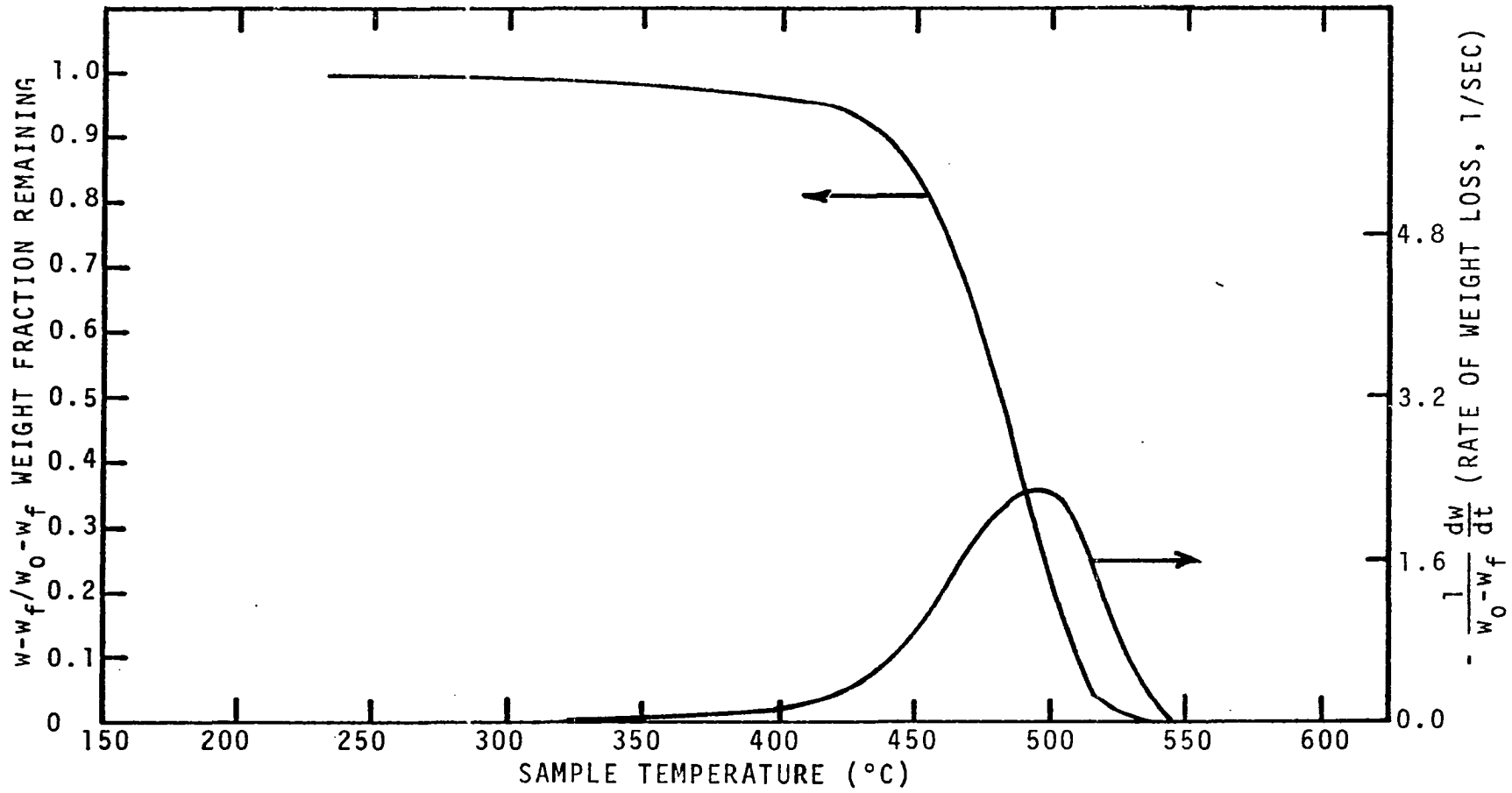

Figure III-16. Weight Loss and Rate of Weight Loss for White Polystyrene. Heating Rate - 160°C/min.

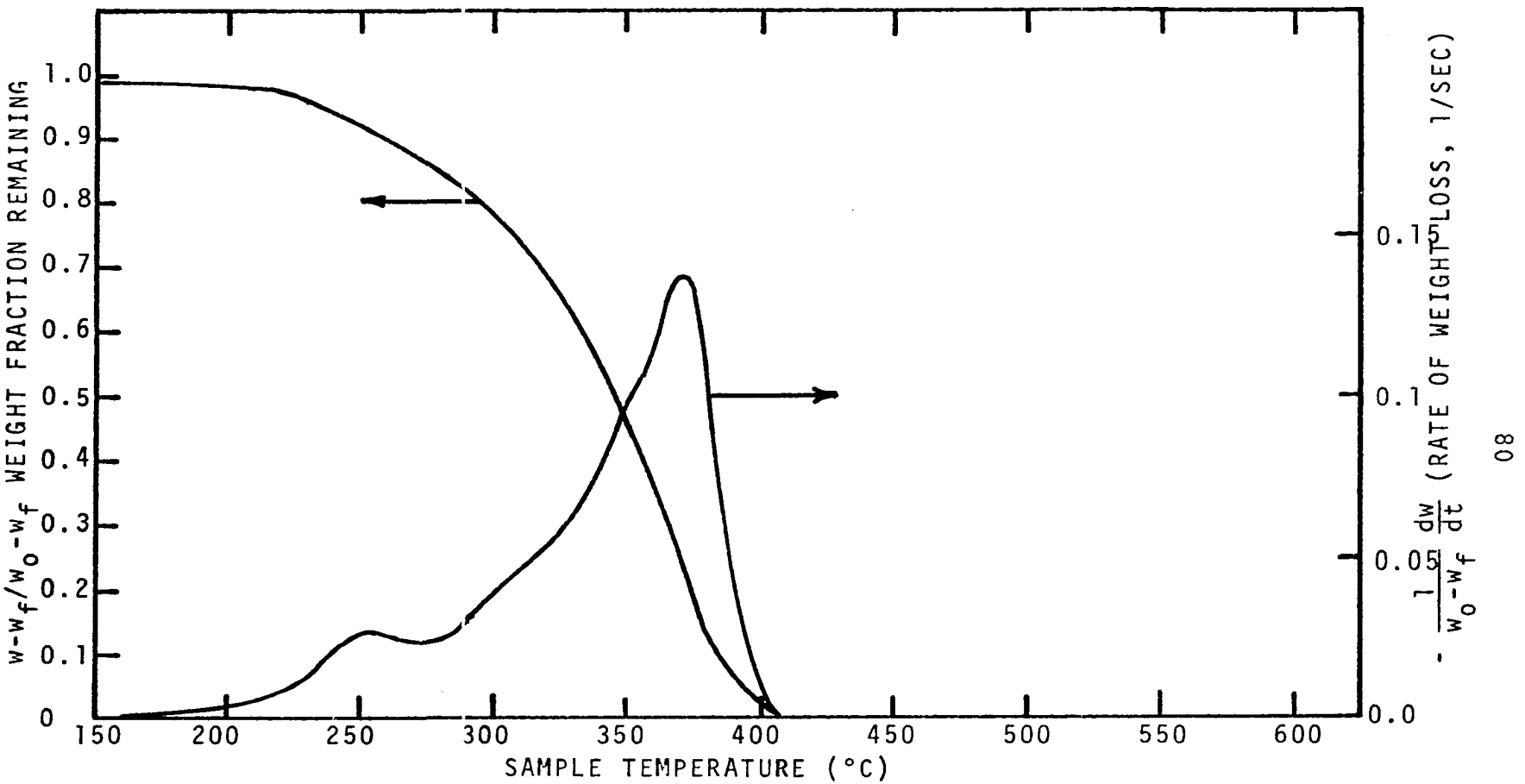

Figure III-17. Weight Loss and Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 10°C/min.

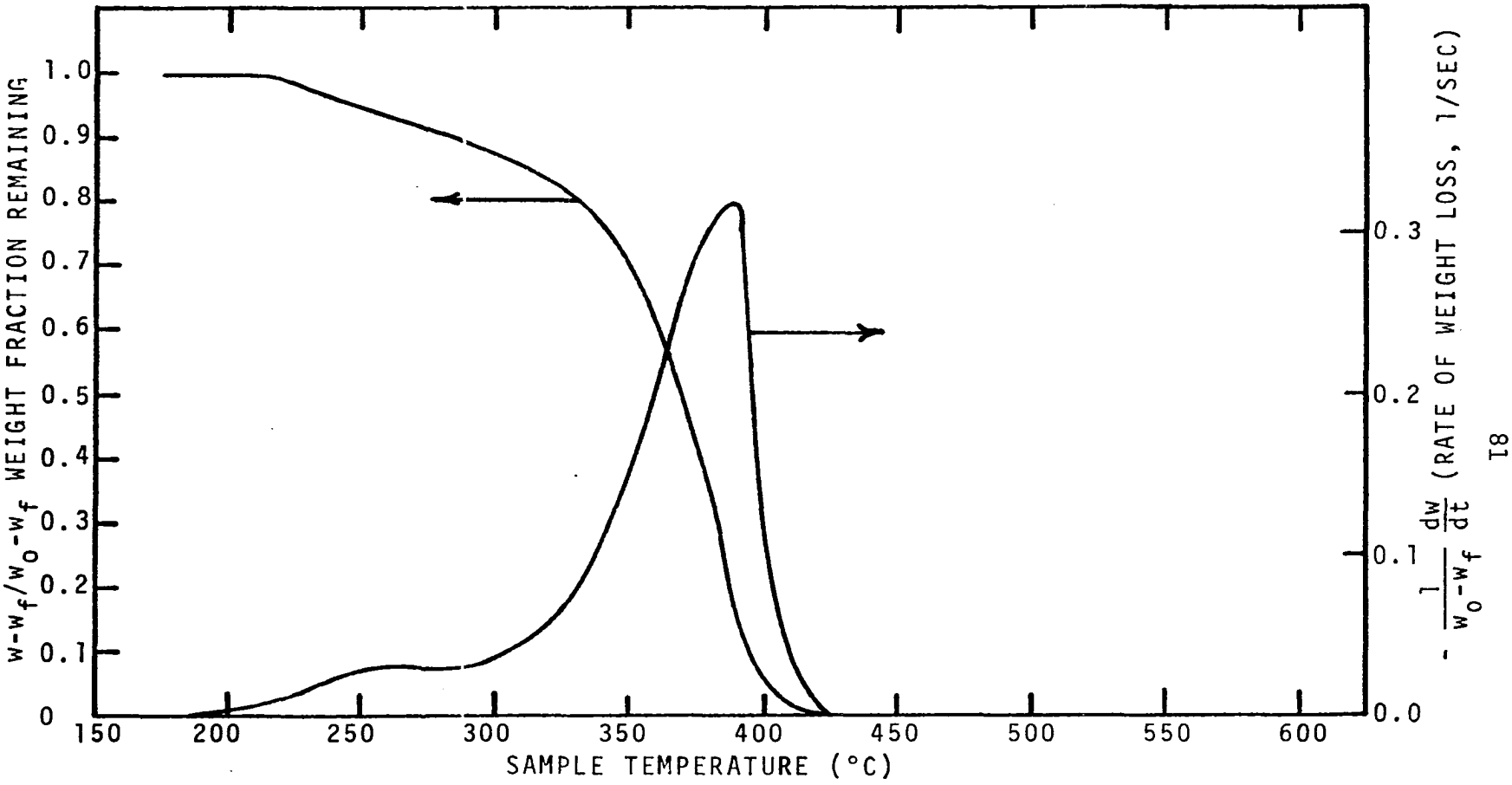

Figure III-18. Weight Loss and Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 20°C/min.

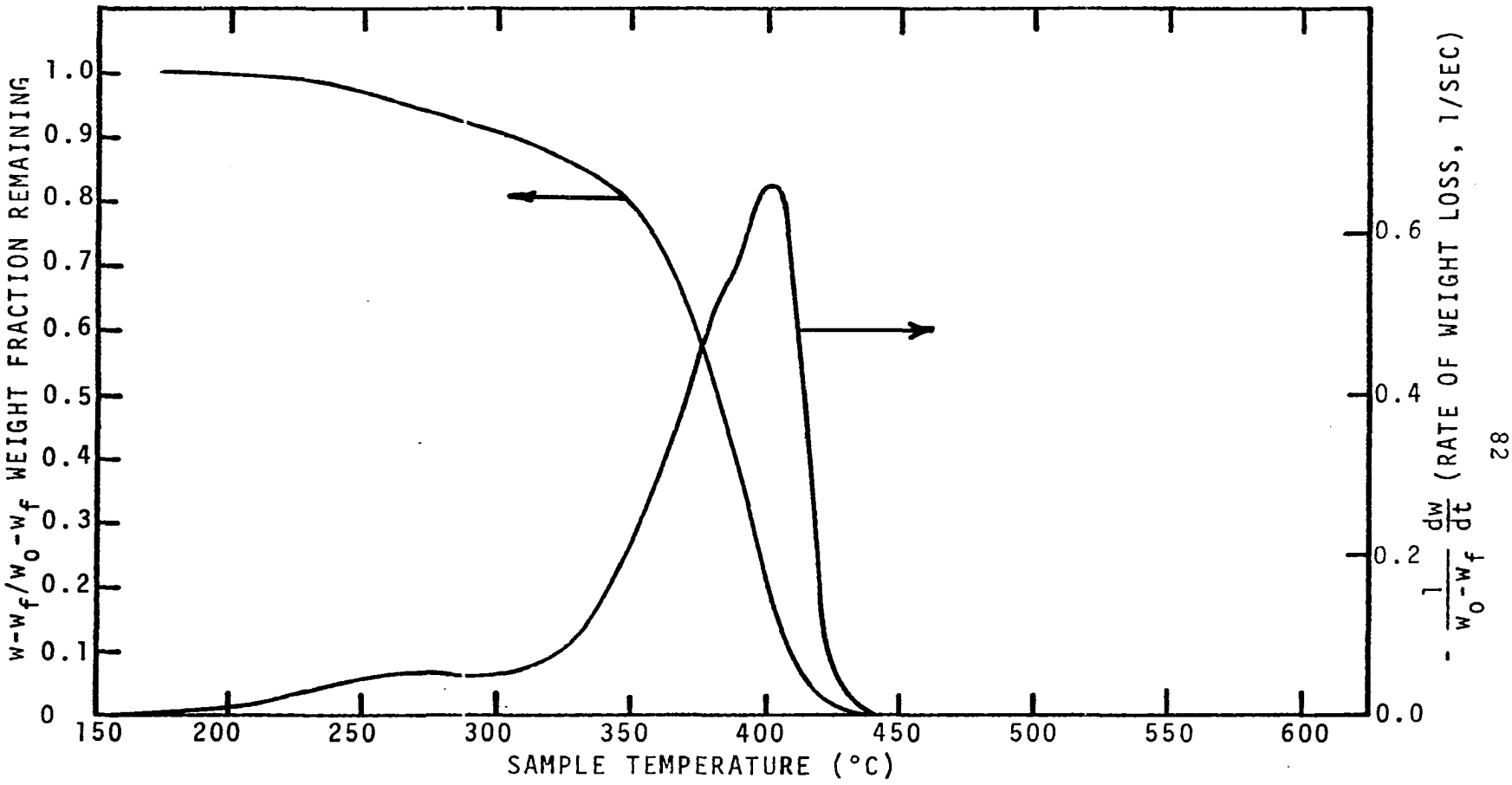

Figure III-19. Weight Loss and Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 40°C/min.

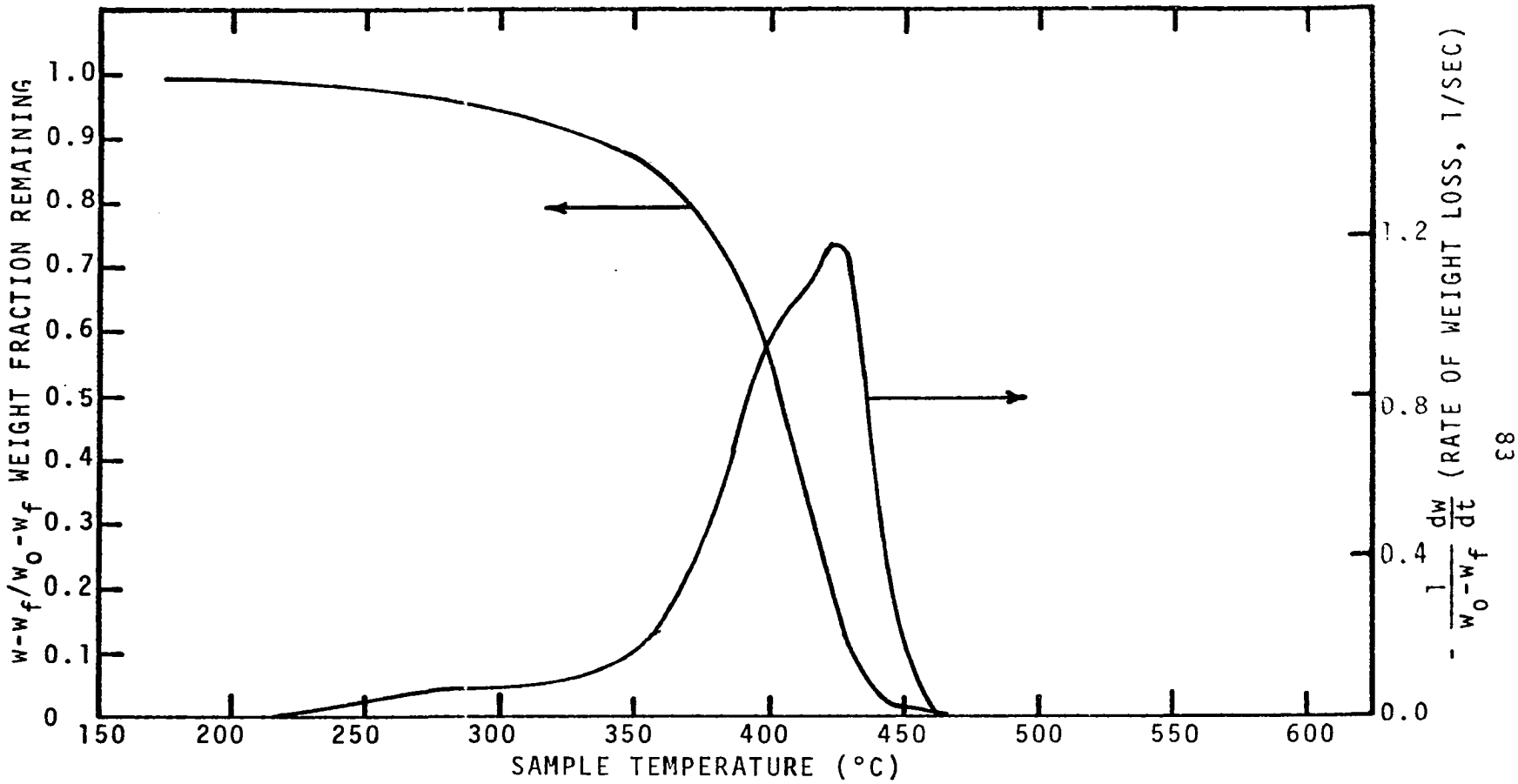

Figure III-20. Weight Loss and Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 80°C/min.

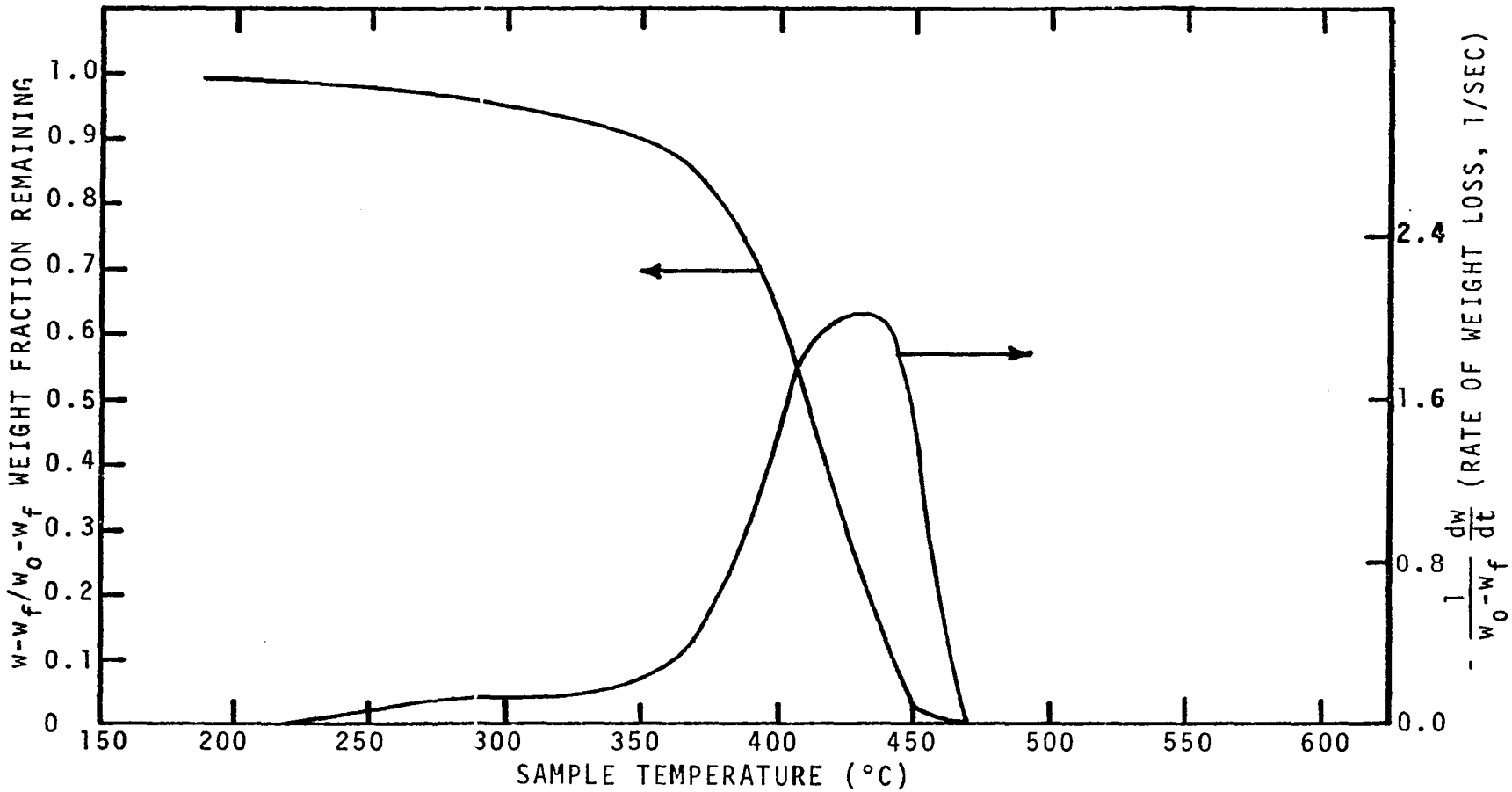

Figure III-21. Weight Loss and Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 160°C/min.

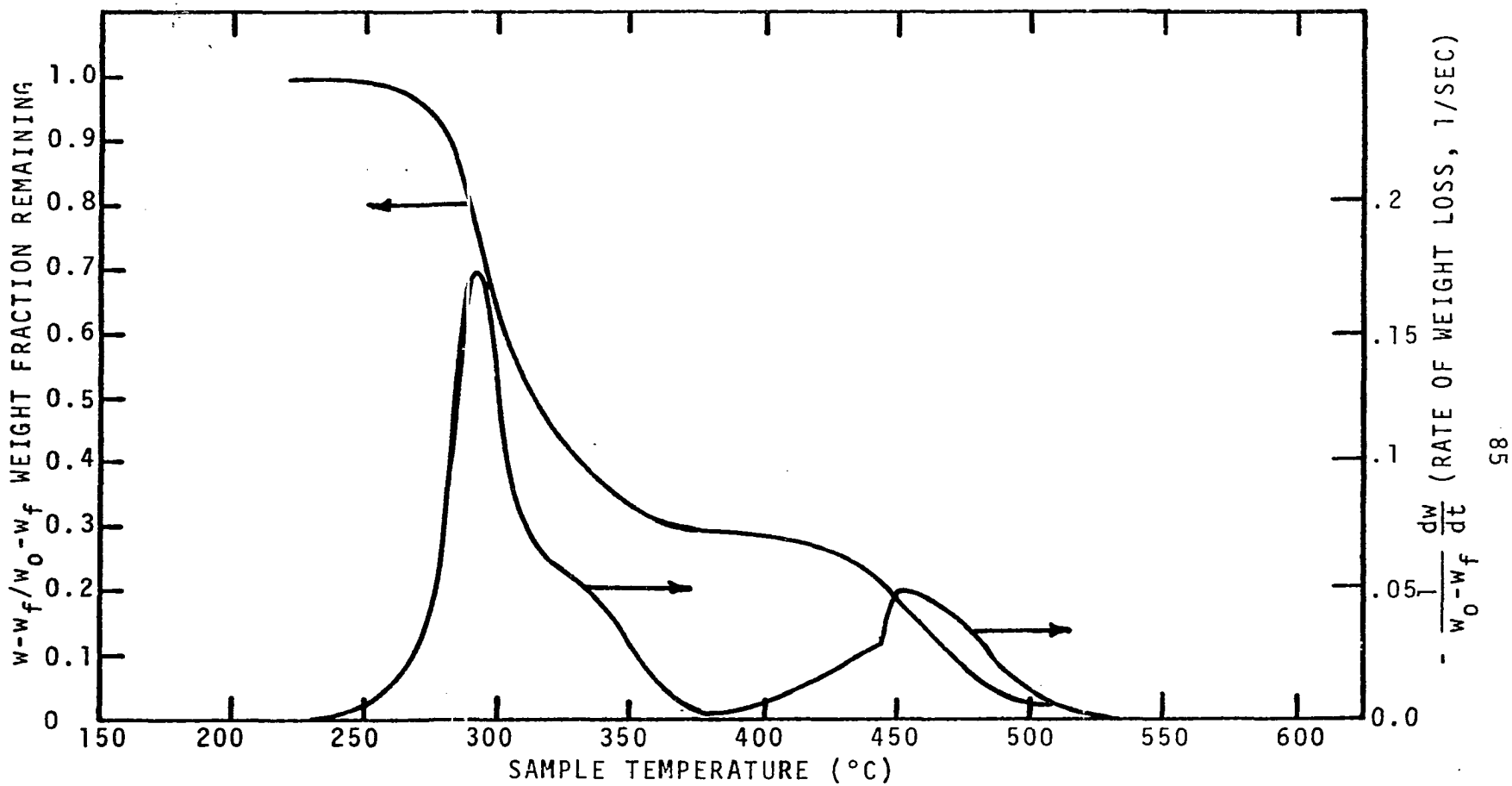

Figure III-22. Weight Loss and Rate of Weight Loss for Unstabilized Polyvinyl Chloride. Heating Rate - 10°C/min.

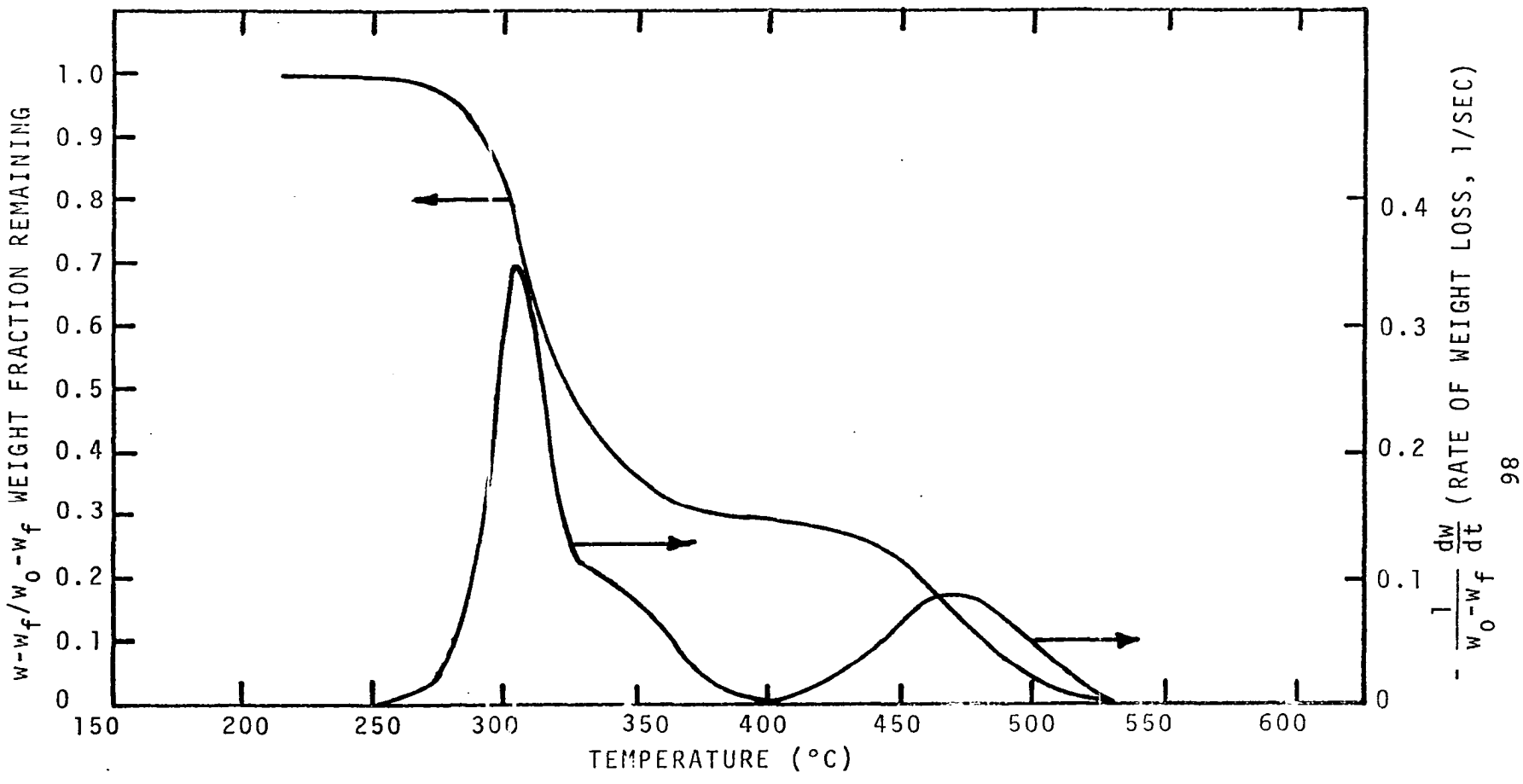

Figure III-23. Weight Loss and Rate of Weight Loss for Unstabilized Polyvinyl Chloride. Heating Rate - 20°C/min.

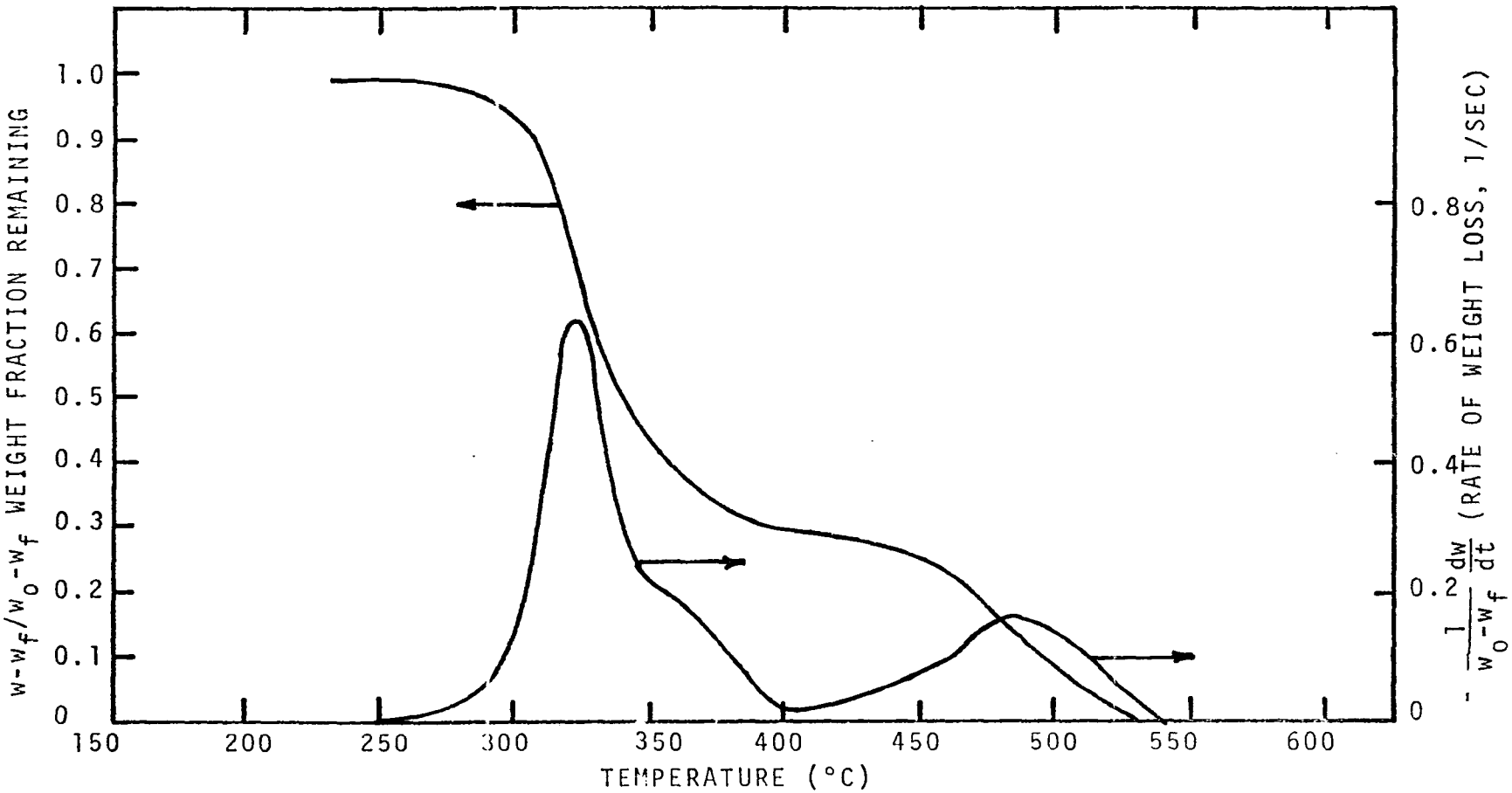

Figure III-24. Weight Loss and Rate of Weight Loss for Unstabilized Polyvinyl Chloride. Heating Rate - 40°C/min.

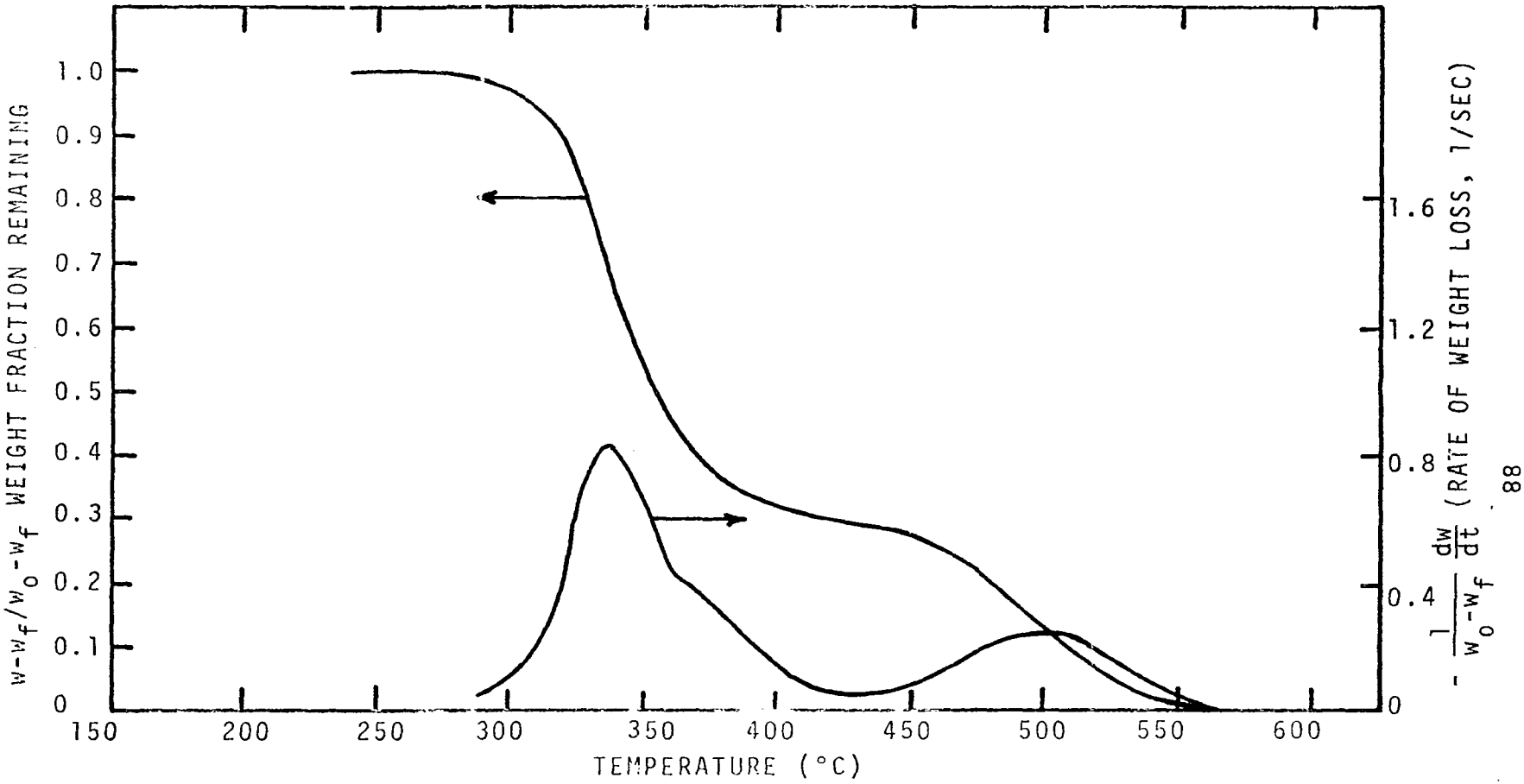

Figure III-25. Weight Loss and Rate of Weight Loss for Unstabilized Polyvinyl Chloride. Heating Rate - 80°C/min.

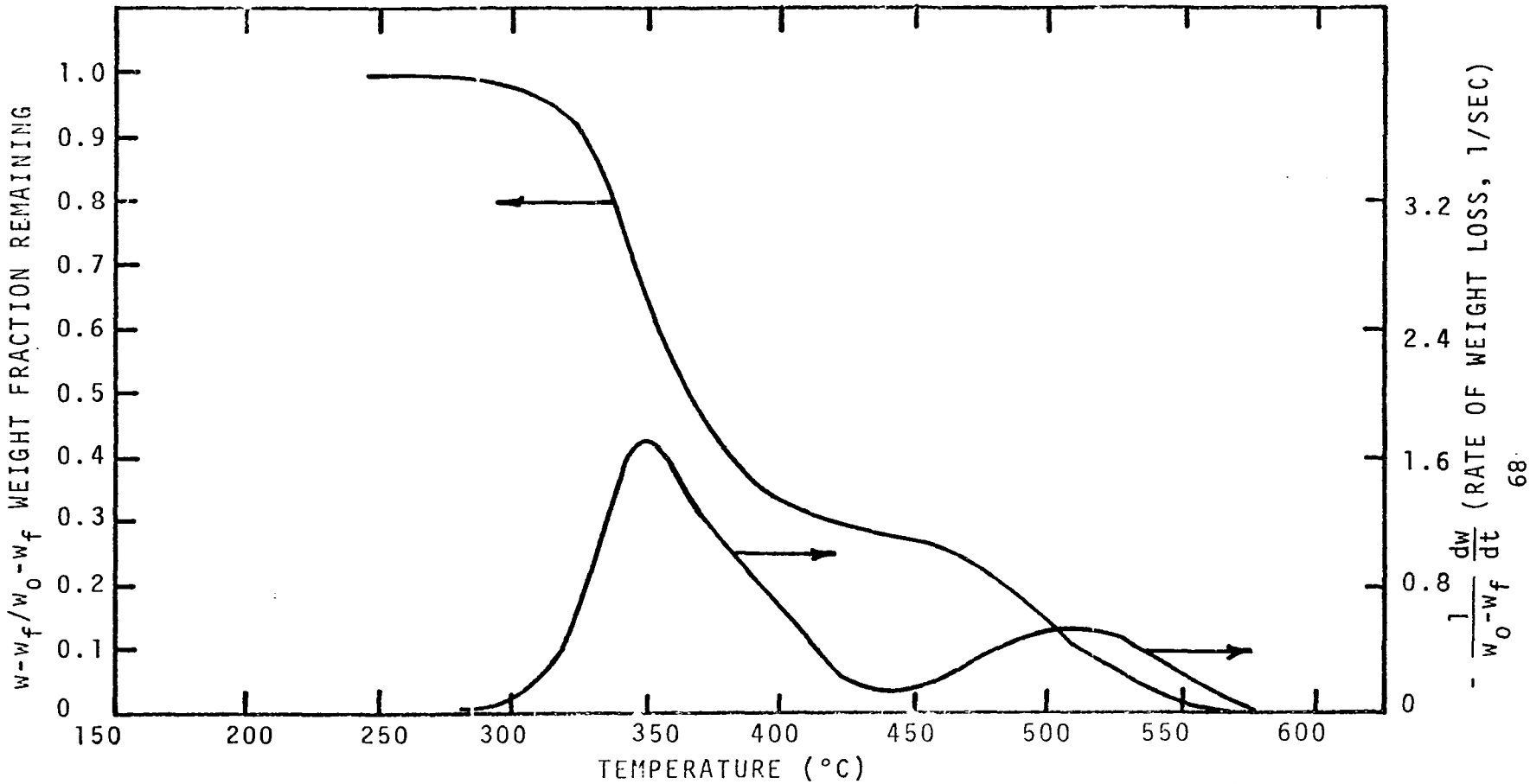

Figure III-26. Weight Loss and Rate of Weight Loss for Unstabilized Polyvinyl Chloride. Heating Rate - 160°C/min.

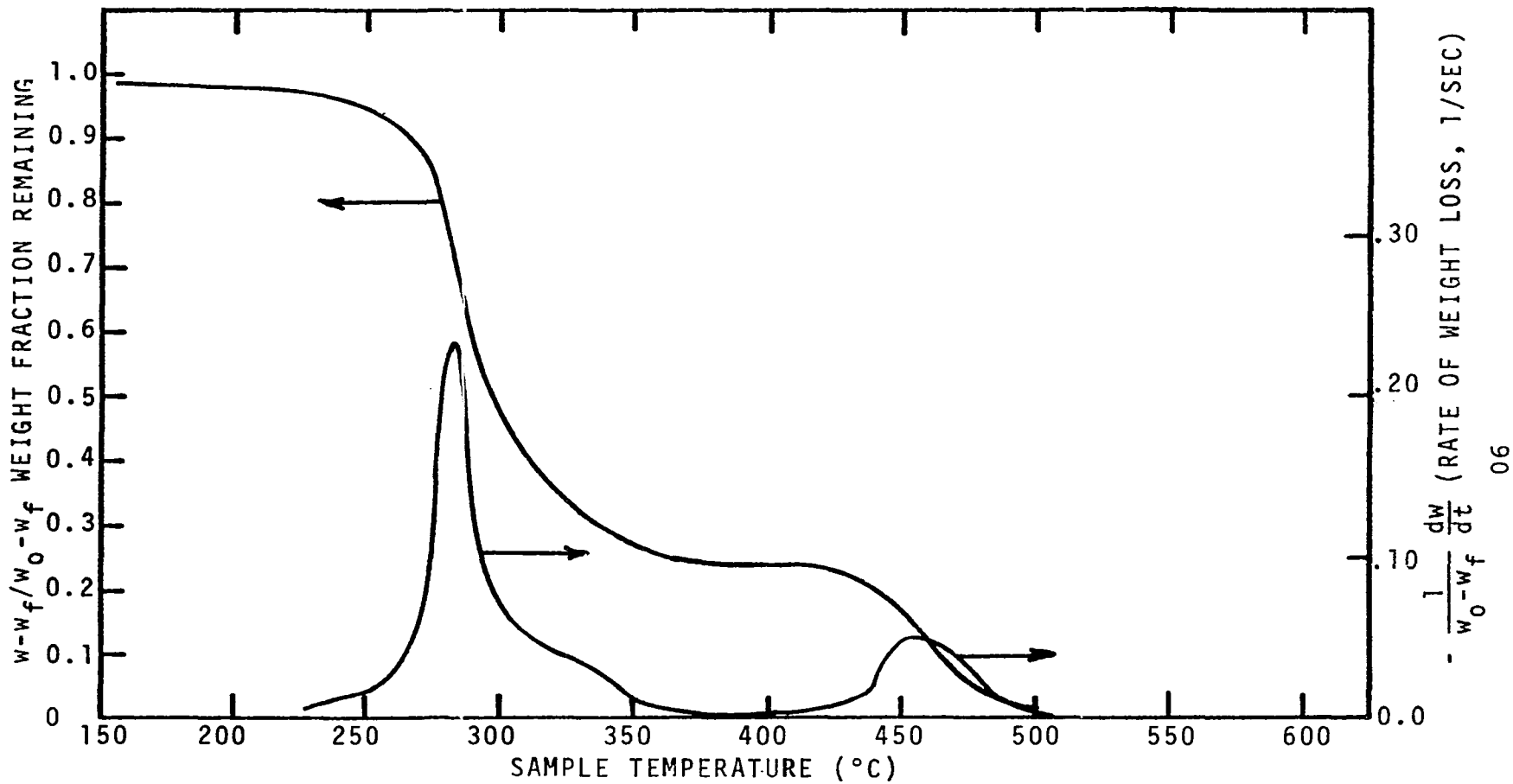

Figure III-27. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 10°C/min.

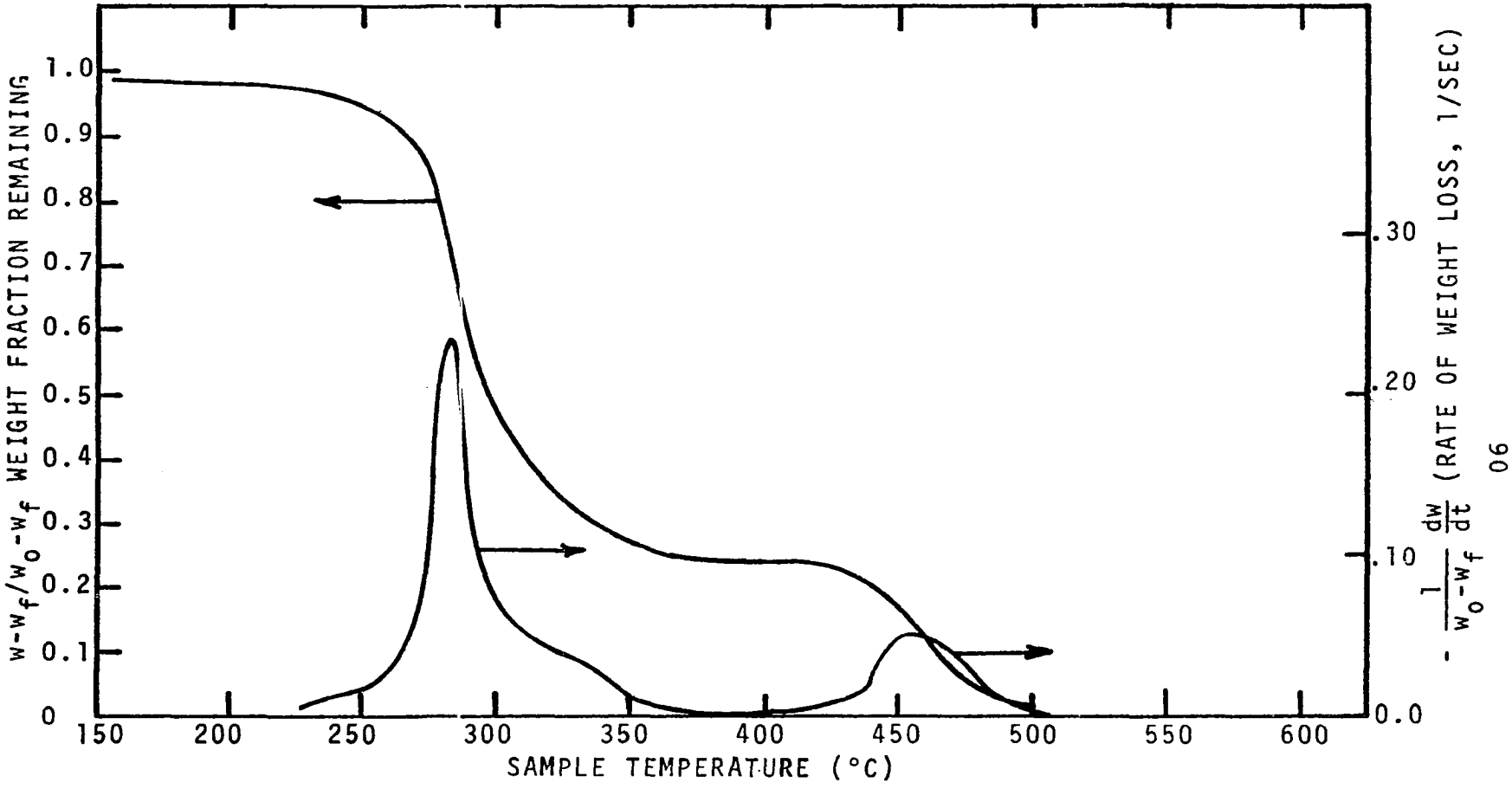

Figure III-27. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 10°C/min.

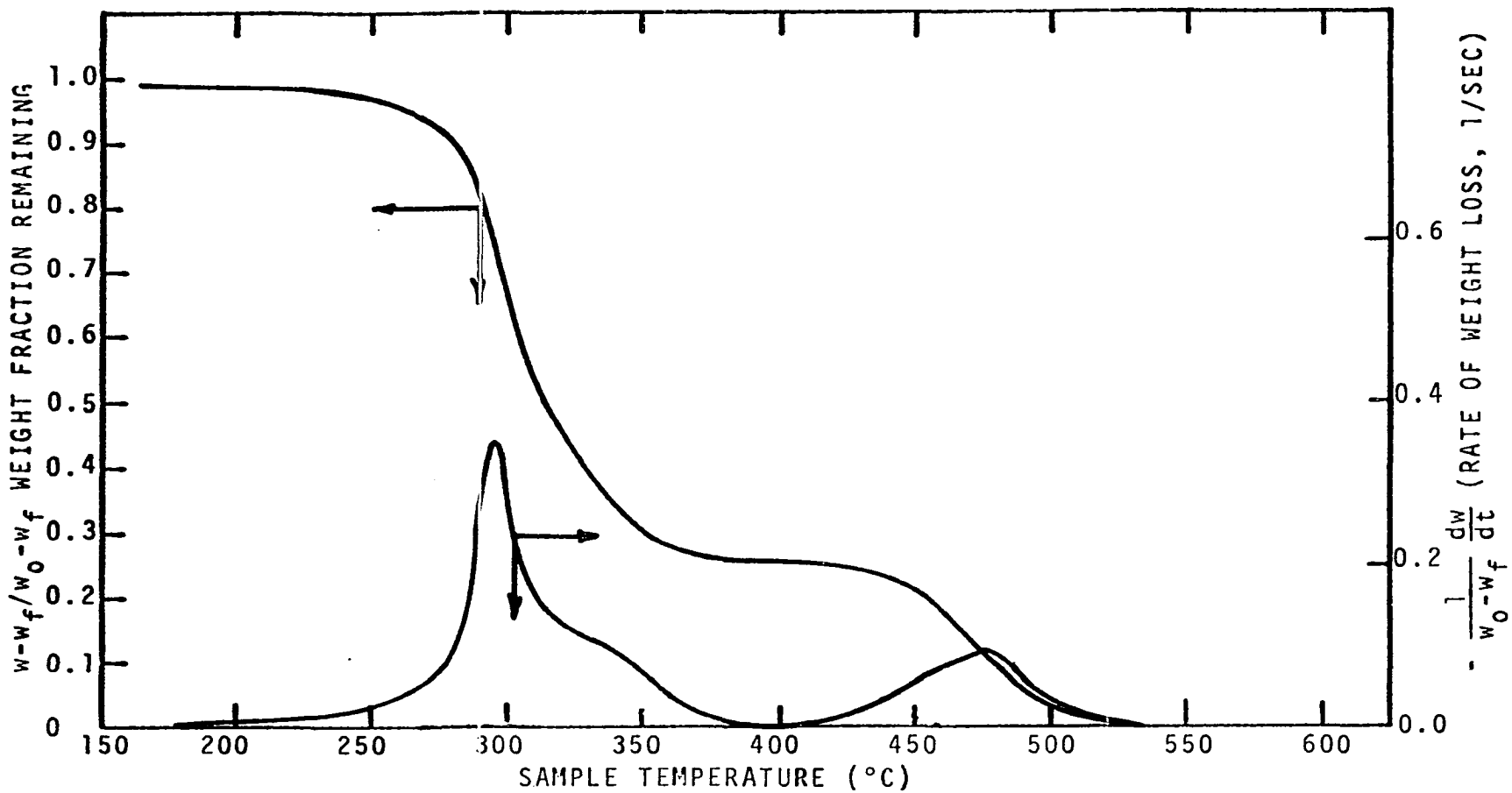

Figure III-28. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 20°C/min.

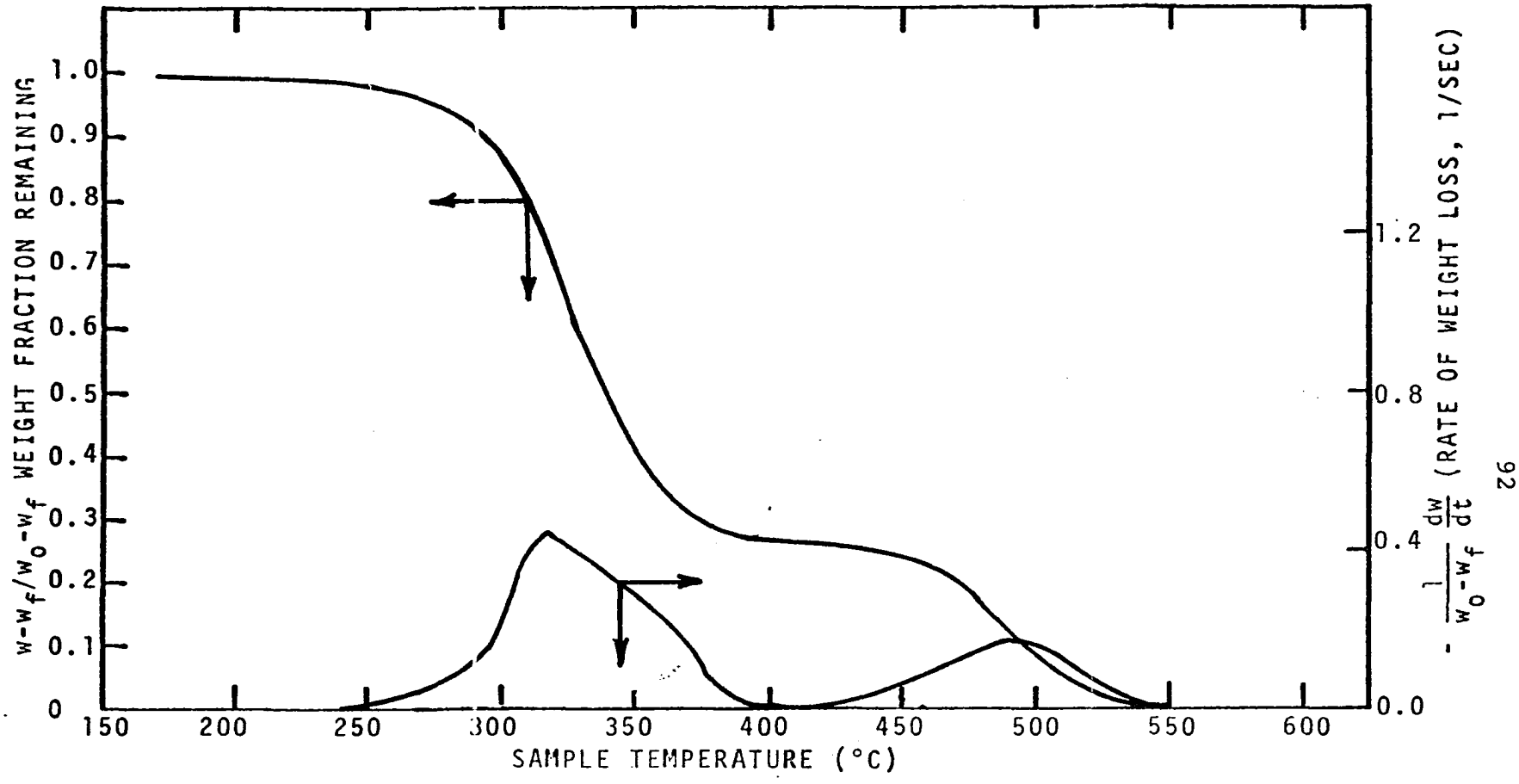

Figure III-29. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 40°C/min.

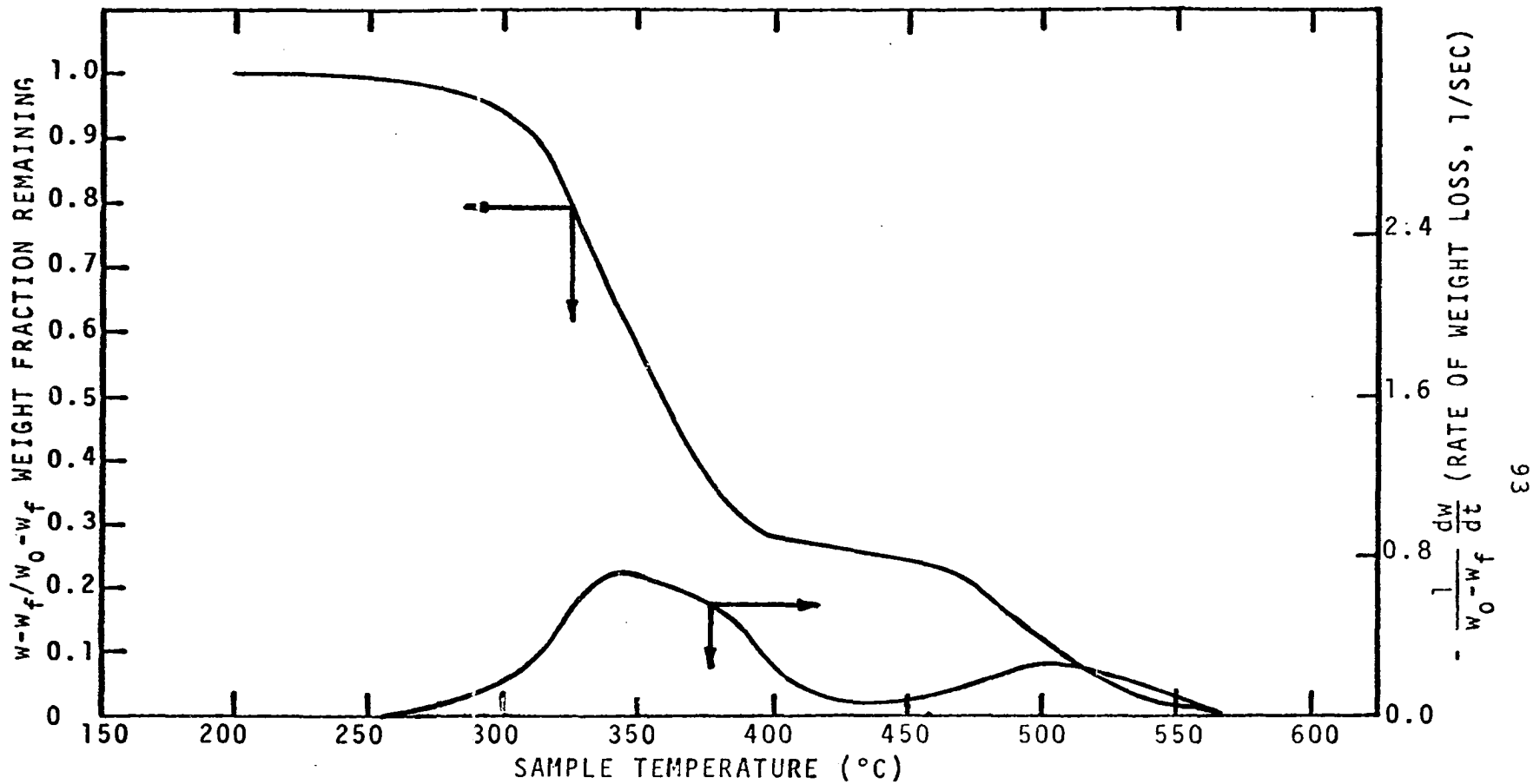

Figure III-30. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 80°C/min.

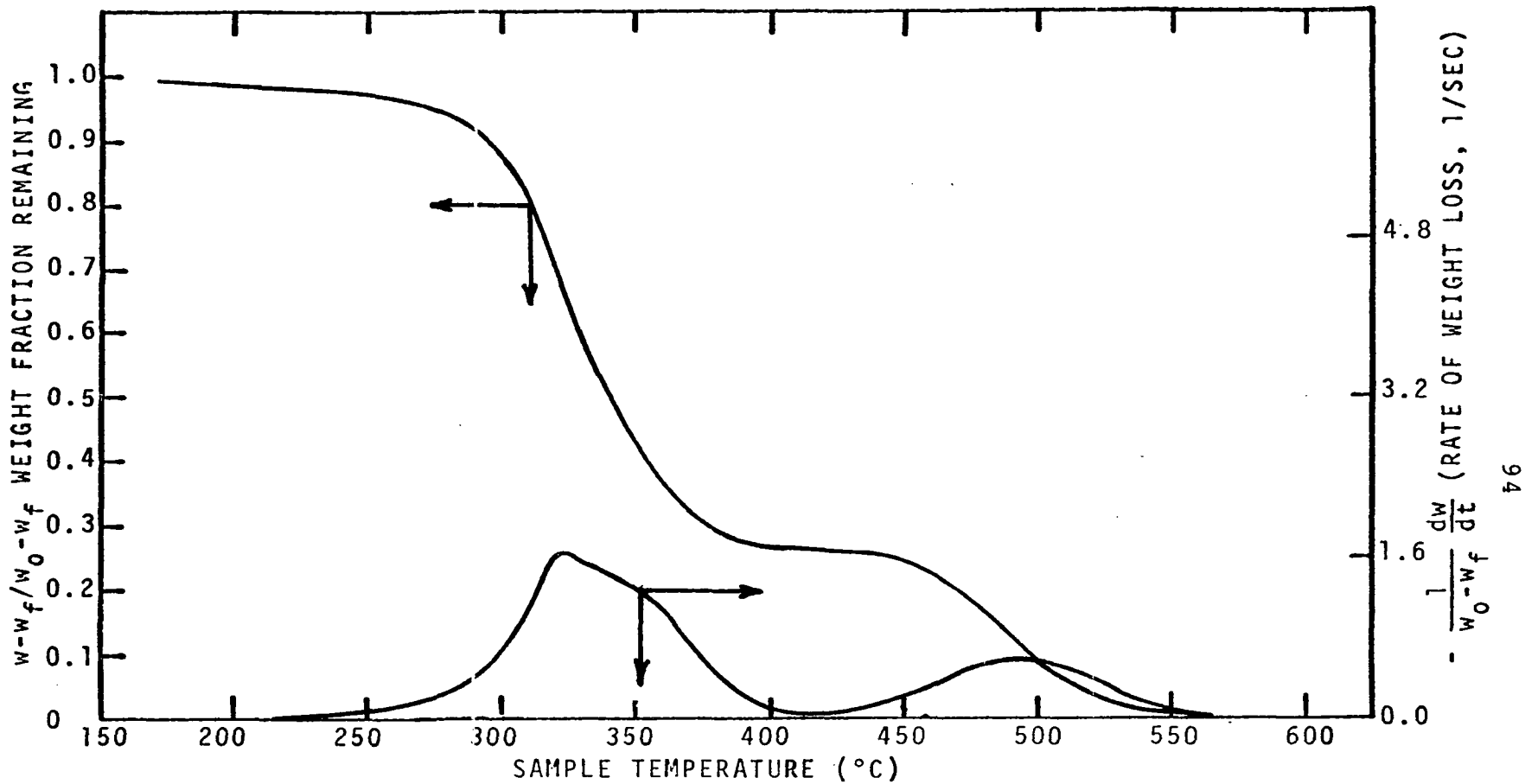

Figure III-31. Weight Loss and Rate of Weight Loss for Clear Polyvinyl Chloride. Heating Rate - 160°C/min.

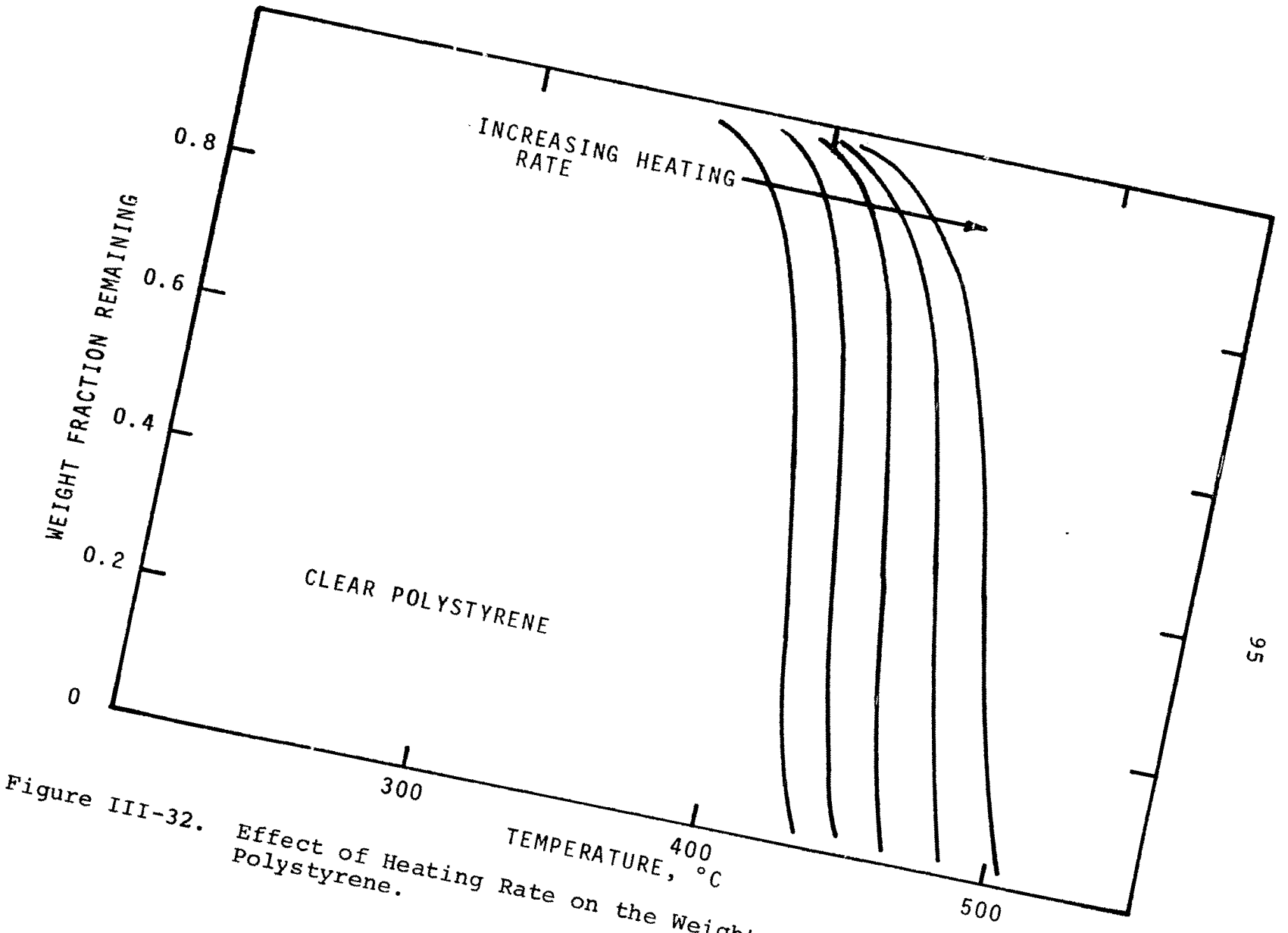

Figure III-32. Effect of Heating Rate on the Weight Loss Kinetics of Clear Polystyrene.

$$-\frac{dW}{dt} = Ae^{-E/RT}(W)^n \qquad \text{(III-4)}$$

The heating rate may be incorporated in Equation III-4 in either of two equivalent ways:

$$-\frac{dW}{dt} = A/\beta e^{-E/RT}\ (W)^n \qquad \text{(III-5)}$$

or

$$-\frac{dW}{dt} = Ae^{-E/R(T_o + \beta t)}\ (W)^n \qquad \text{(III-6)}$$

where β is the heating rate. Equation III-5 may be integrated to give

$$\int_{1.0}^{W} -\frac{dW}{W^n} = A/\beta \int_{T_o}^{T} e^{-E/RT}\ dT \qquad \text{(III-7)}$$

As the heating rate increases the term A/β will decrease. Thus to achieve any specified weight loss, W, it can be seen from Equation III-7 that a higher temperature is required.

The effect of an increasing heating rate on the rate of weight loss may be examined in Figure III-33. These curves not only shift toward higher temperatures but the maximum rate of weight loss with respect to temperature shows a steady decrease. Equation III-5 may be differentiated with respect to temperature to obtain

$$-\frac{d^2W}{dT^2} = E/RT^2 + \frac{n}{W}\frac{dW}{dT} \qquad \text{(III-8)}$$

At the maximum rate of weight loss this is set equal to zero to give

$$\left(-\frac{dW}{dT}\right)_{max} = \frac{E(W)_{max}}{nRT^2_{max}} \qquad \text{(III-9)}$$

Equation III-9 shows that $(dW/dT)_{max}$ will decrease due to the increase in T_{max} as the heating rate is increased, provided that the maximum rate of weight loss occurs near the same fractional weight remaining for each rate.

The energy changes associated with the thermal decomposition of the two polystyrene samples and PMMA were studied in a flowing nitrogen atmosphere at heating rates of 10, 20 40, and 80°C/min. 80°C/min is the maximum rate of heating available on the DSC-1b. PVC was not studied on the DSC because of the maximum temperature limit of 500°C. At the heating rates studied PVC does not decompose completely until well above this temperature. No heat transfer effects dependent on sample size were observed in these studies with samples as large as 12.00 mg; however, the larger samples did cause some difficulties in reproducing the isothermal baselines due to condensation of volatiles on the radiation domes. All energy changes for these two polymers in a nitrogen atmosphere were endothermic. The results of this portion of the experimental studies are shown in Figures III-34 through III-45. The rate of weight loss is shown with the rate of energy change on these figures for comparative purposes. For the most part the dE_d/dt curves show the same general characteristics as the dW/dt curves. E_d is the energy attributed to decomposition. These characteristics will be discussed in the next chapter. The dE_d/dt curves, however, show a consistant lag relative to the dW/dt curves. Flynn (33) has

demonstrated that the DSC-1b can have a time lag of up to twelve seconds at the heating rates studied here. It is felt that the lag in the dE_d/dt curves, relative to the dW/dt curves, is due to this internal time lag of the DSC-1b. While this time lag does not affect the determination of transition energies, it would have to be accounted for in the determination of transition temperatures or in the calculation of kinetic parameters based on DSC data. Kinetic parameters presented in this work are based on TGA data and are not affected by the time lag.

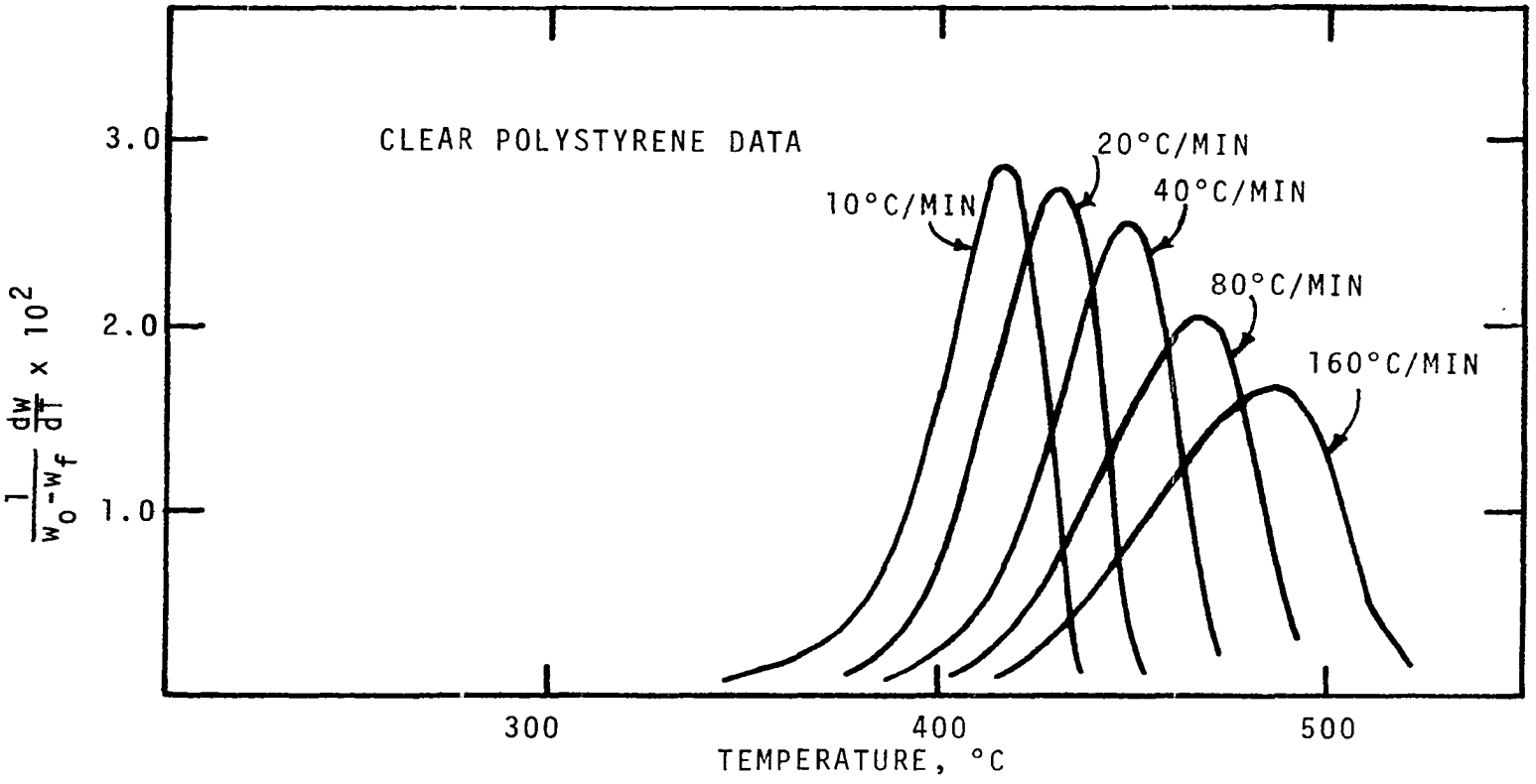

Figure III-33. Effect of Heating on the Rate of Weight Loss of Clear Polystyrene.

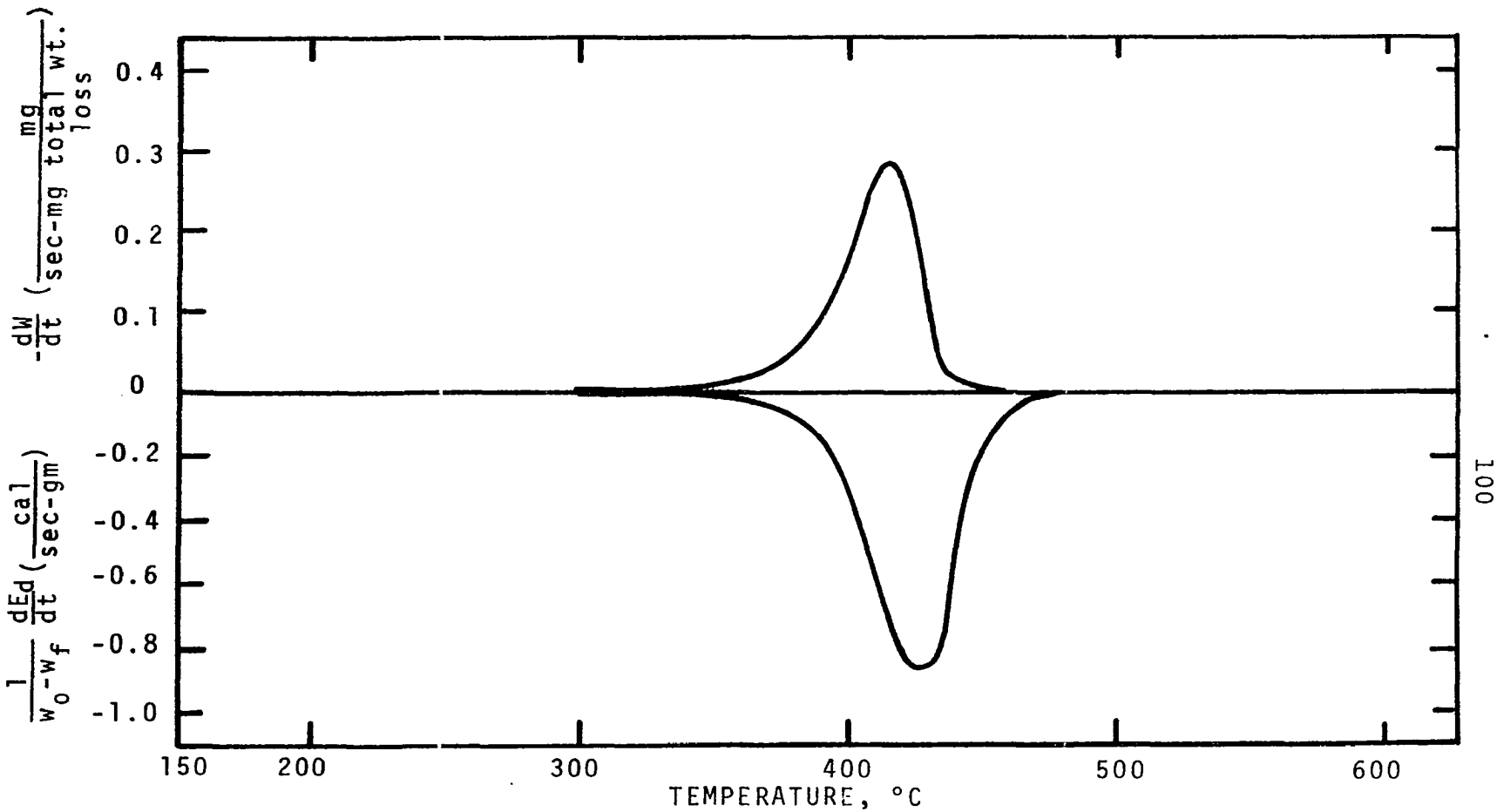

Figure III-34. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Clear Polystyrene. Heating Rate = 10°C/min.

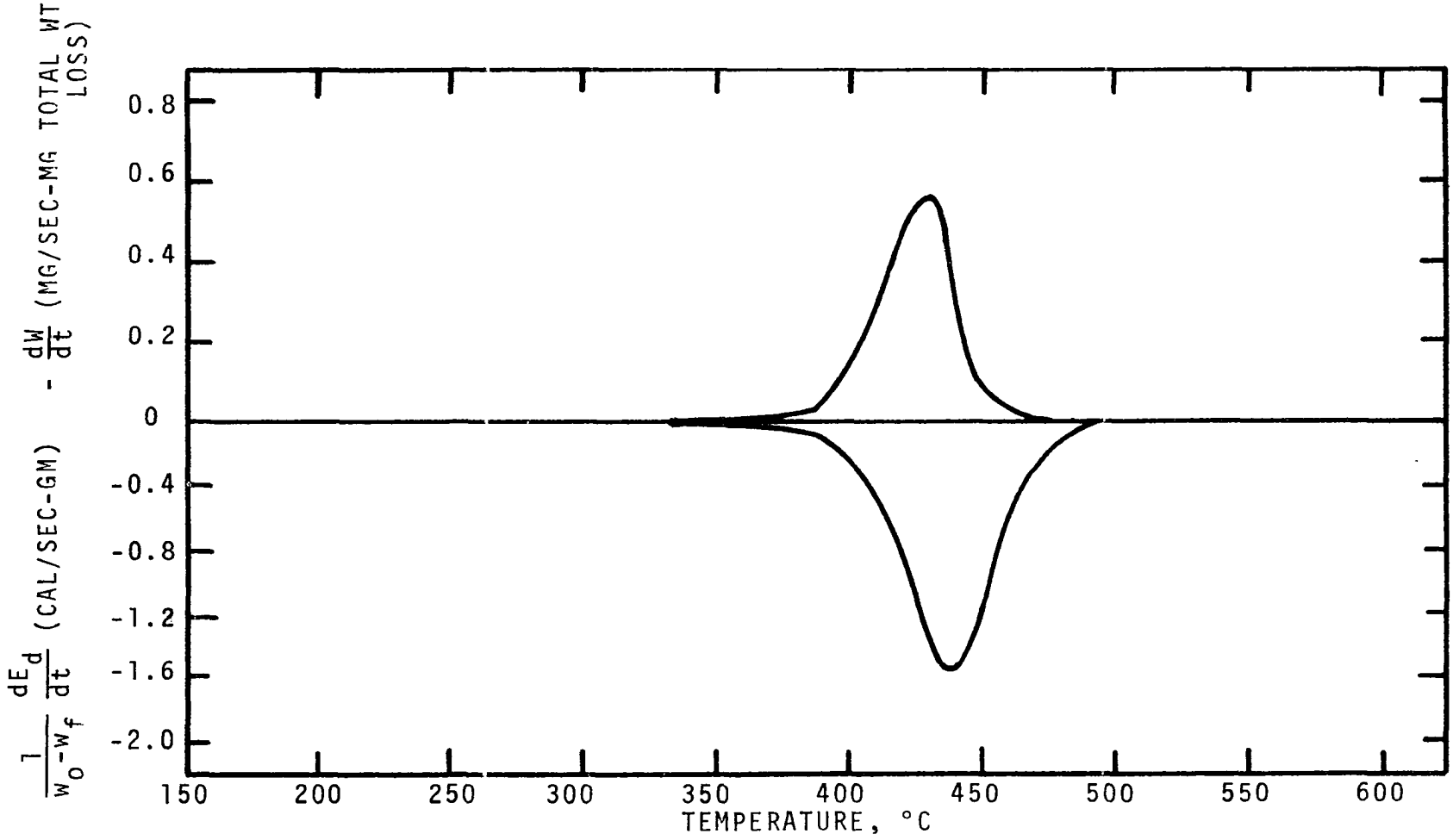

Figure III-35. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Clear Polystyrene. Heating Rate - 20°C/min.

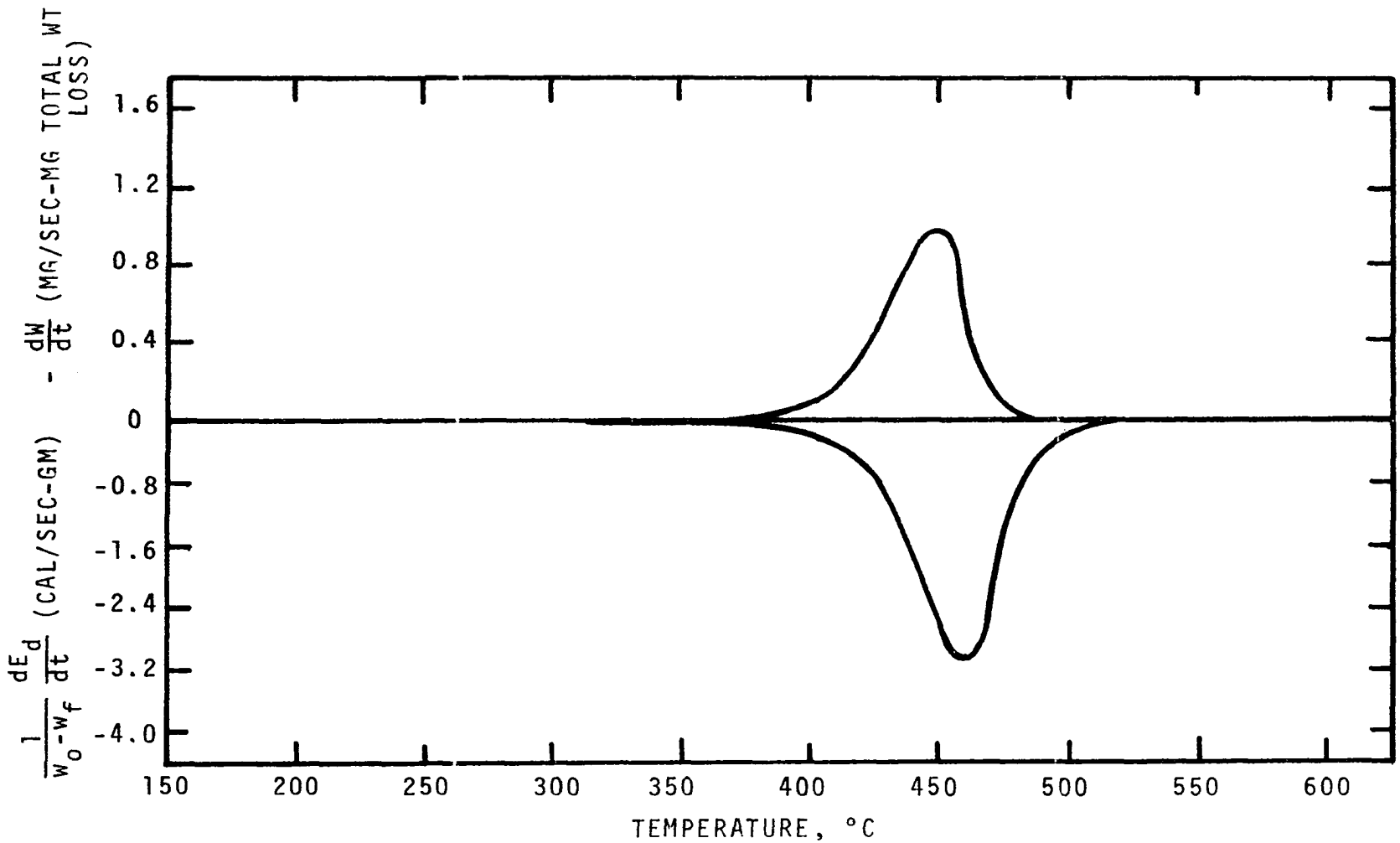

Figure III-36. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Clear Polystyrene. Heating Rate - 40°C/min.

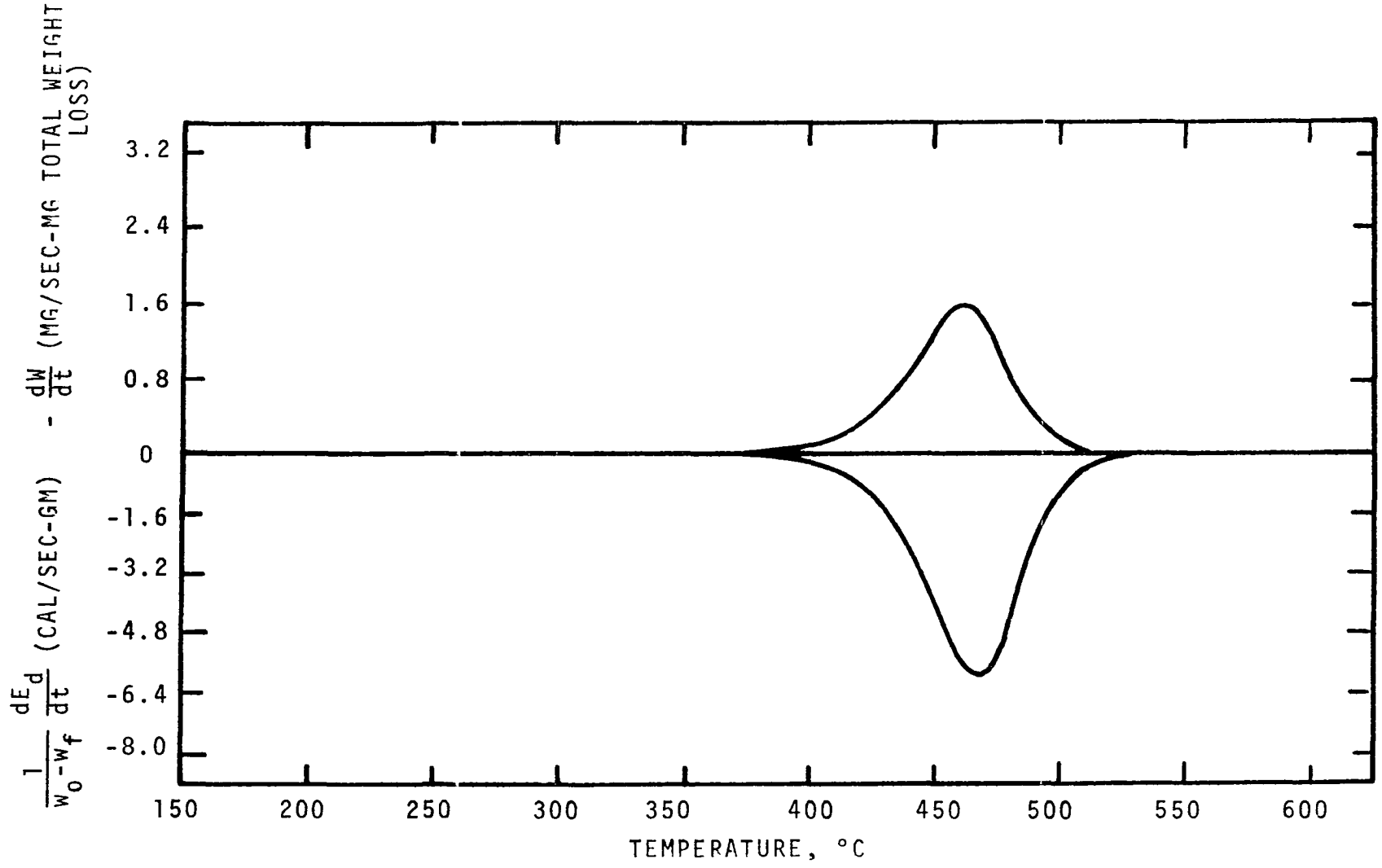

Figure III-37. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Clear Polystyrene. Heating Rate - 30°C/min.

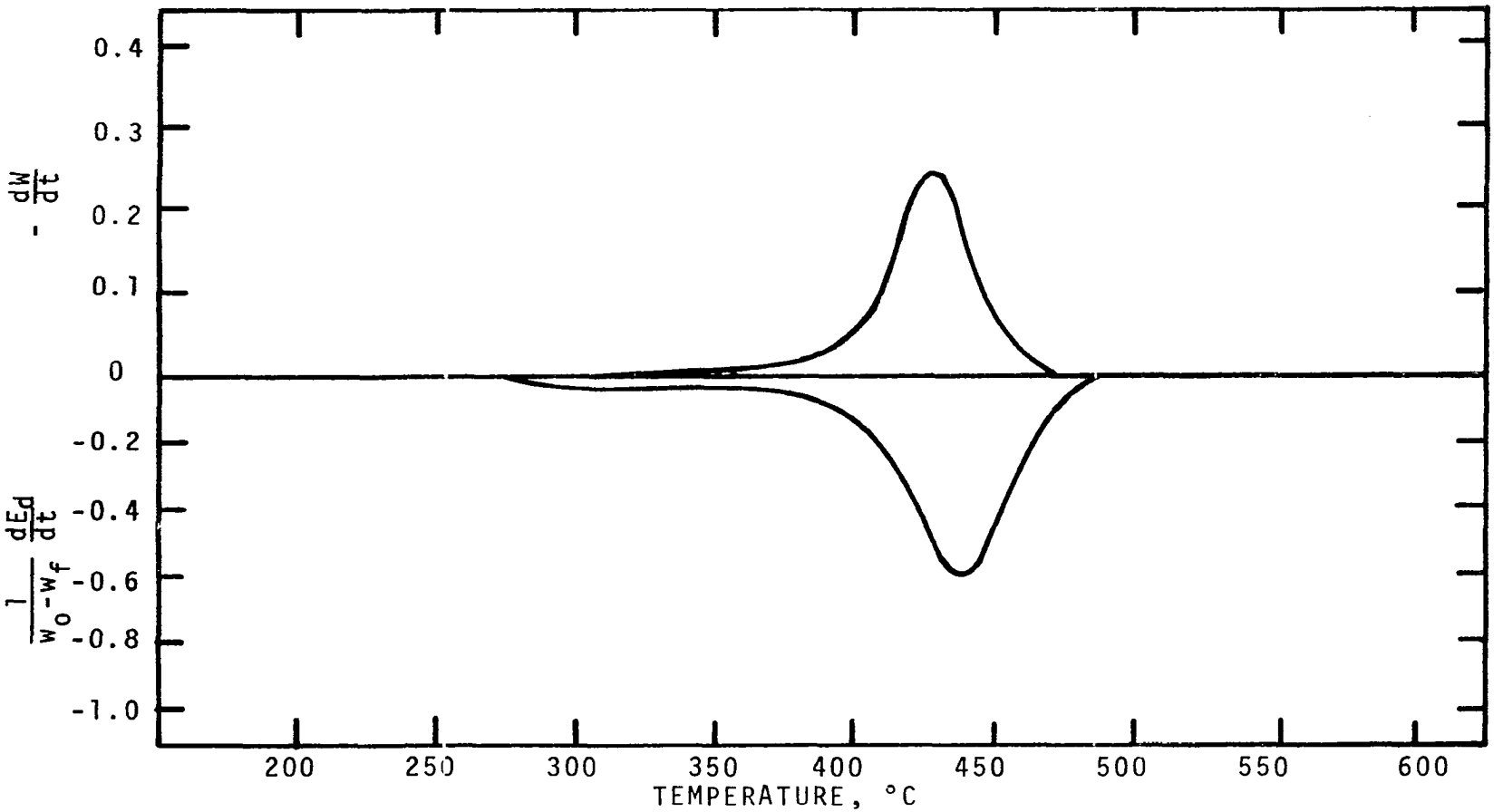

Figure III-38. Comparison of Rate of Energy Change with the Rate of Weight Loss for White Polystyrene. Heating Rate 10°C/min.

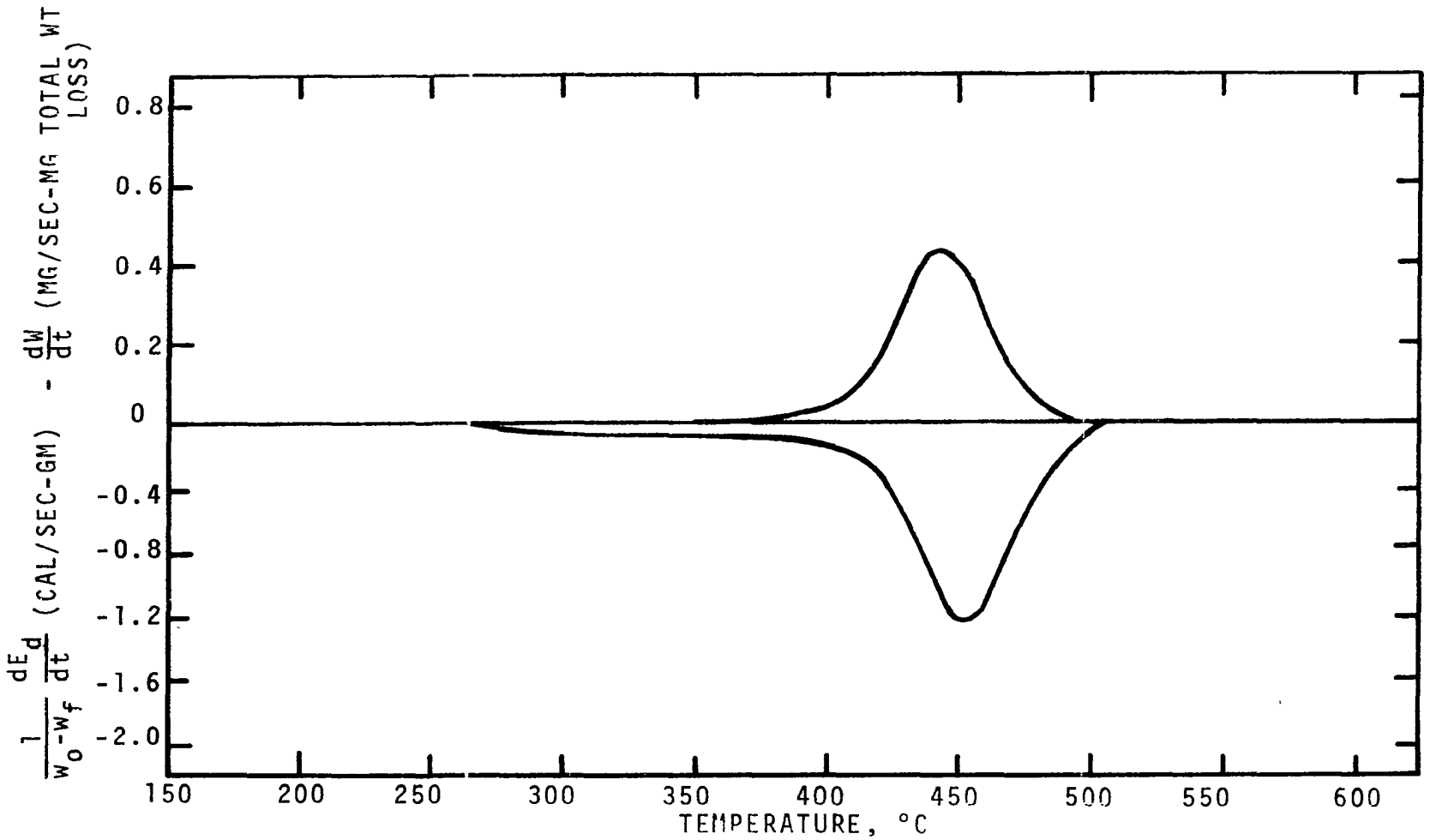

Figure III-39. Comparison of the Rate of Energy Change with the Rate of Weight Loss for White Polystyrene. Heating Rate - 20 °C/min.

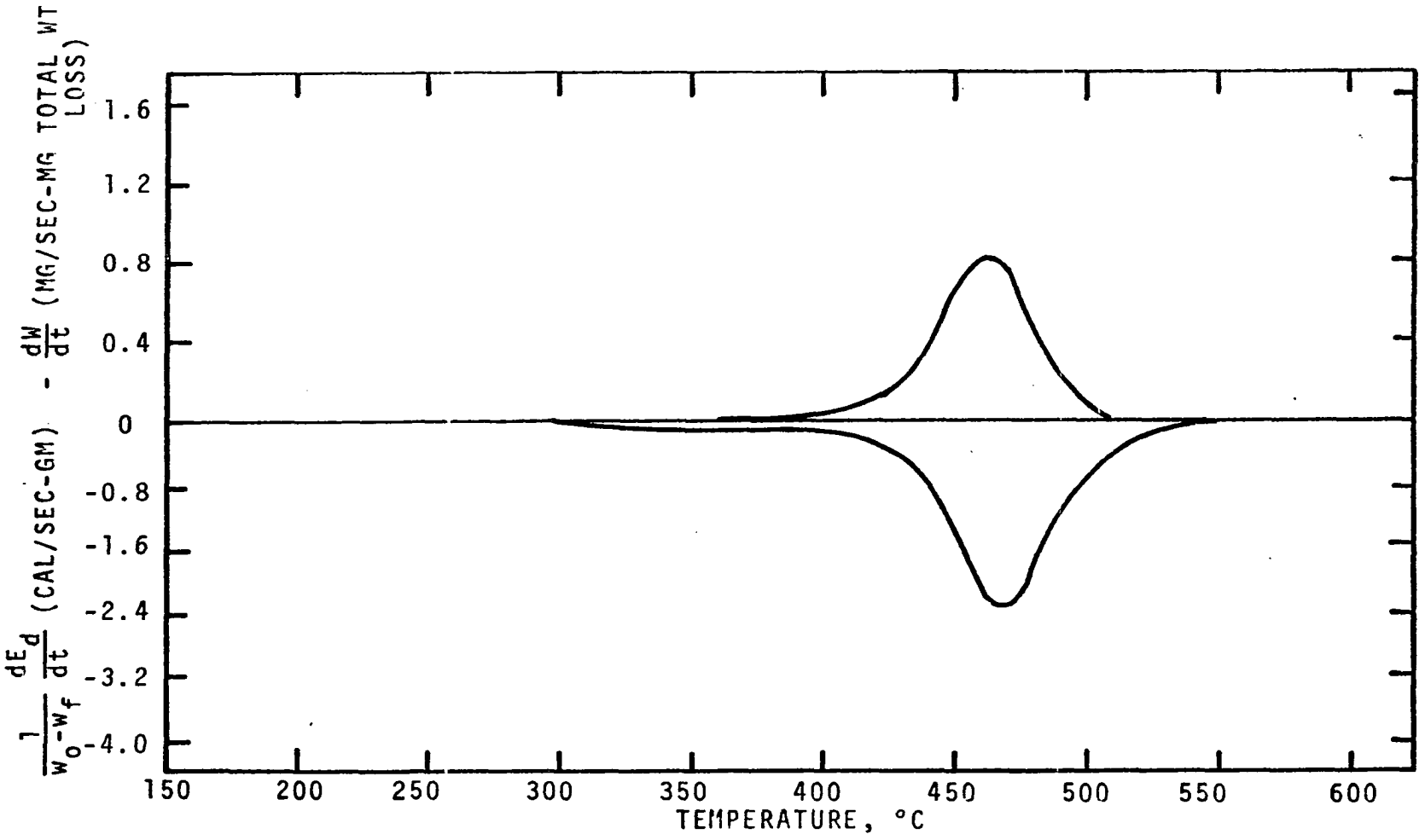

Figure III-40. Comparison of the Rate of Energy Change with the Rate of Weight Loss for White Polystyrene. Heating Rate - 40°C/min.

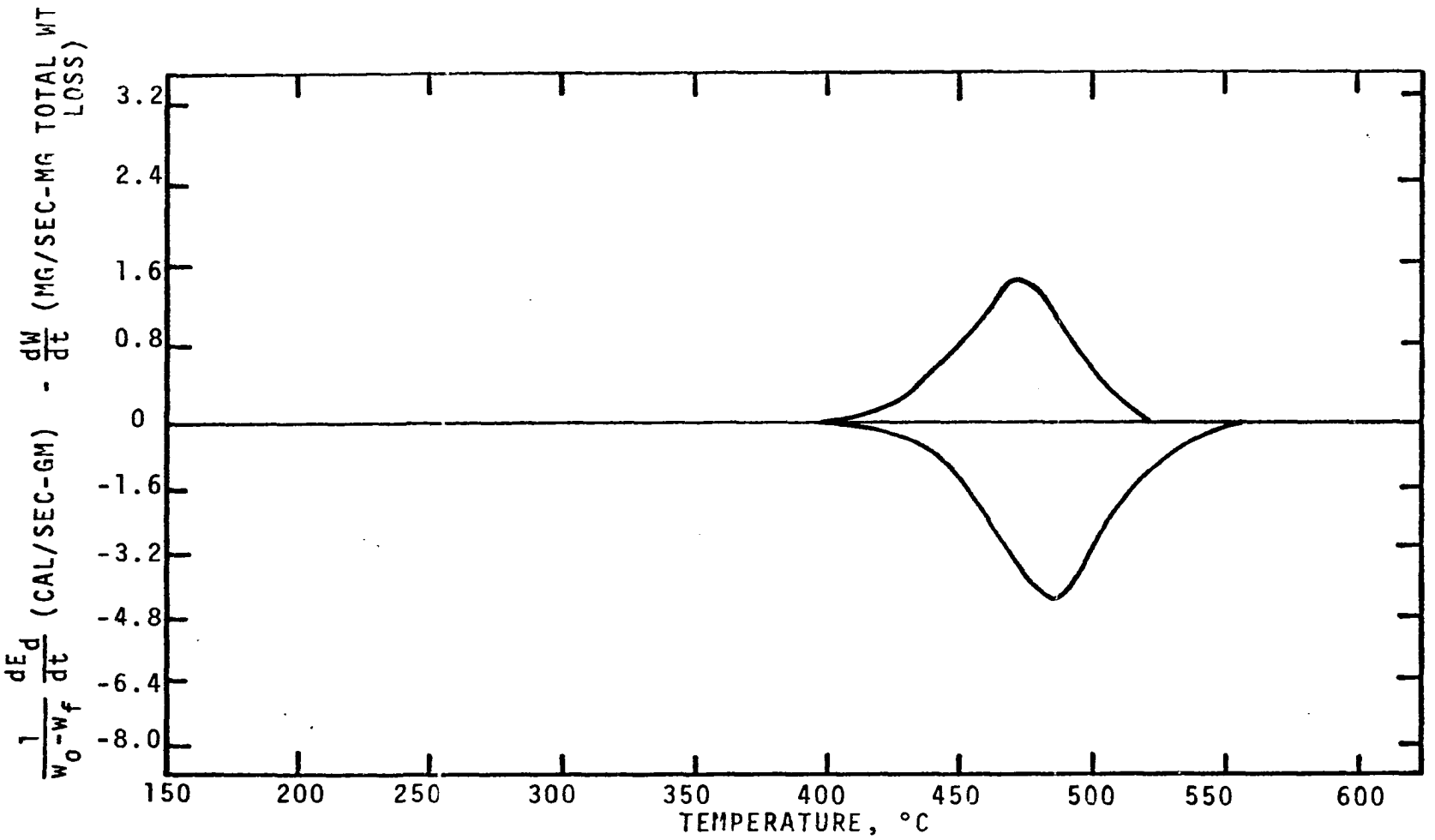

Figure III-41. Comparison of the Rate of Energy Change with the Rate of Weight Loss for White Polystyrene. Heating Rate - 80°C/min.

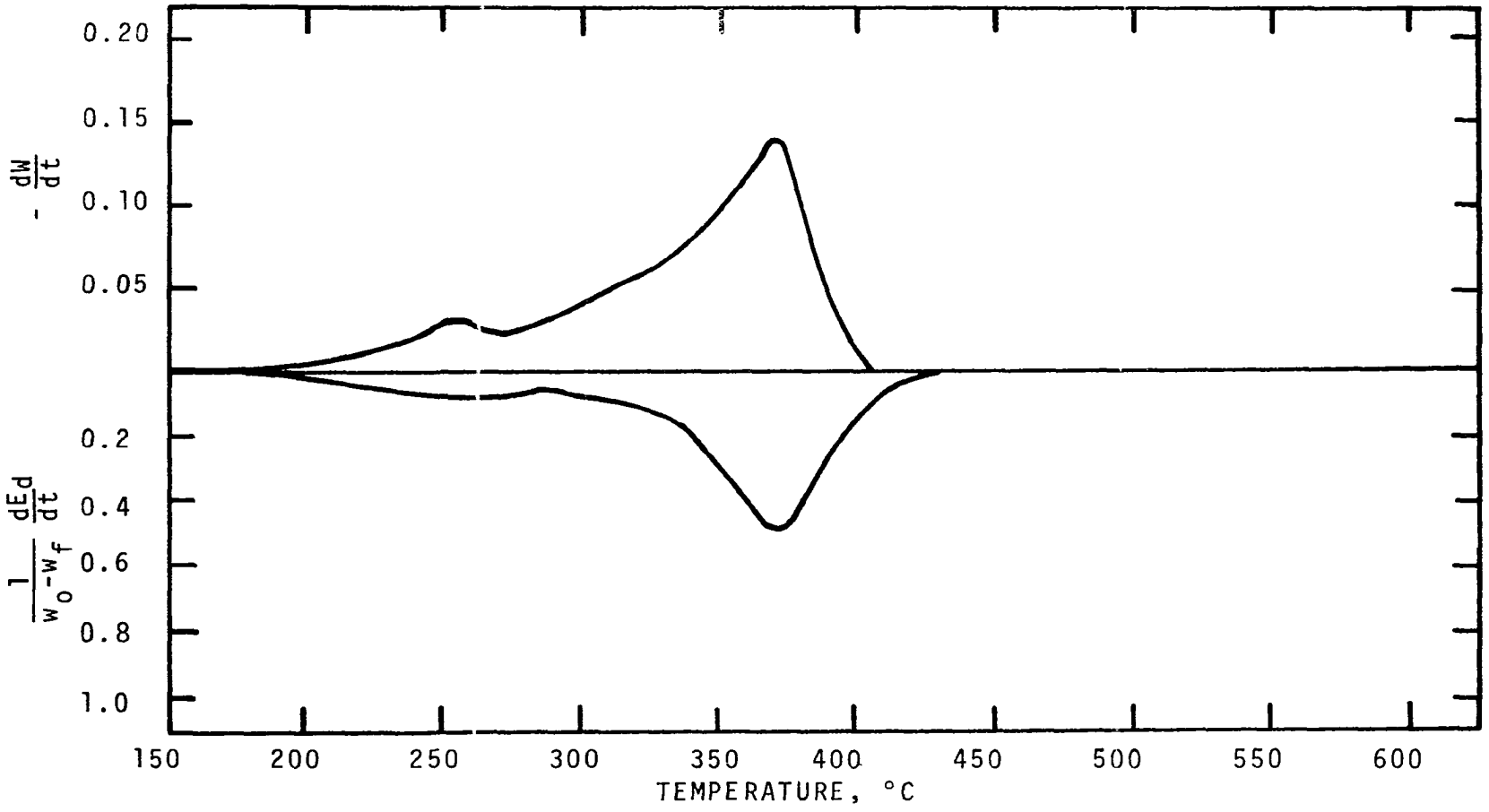

Figure III-42. Comparison of the Rate of Energy Change With the Rate of Weight Loss for Polymethylmethacrylate. Heating Rate-10°C/min.

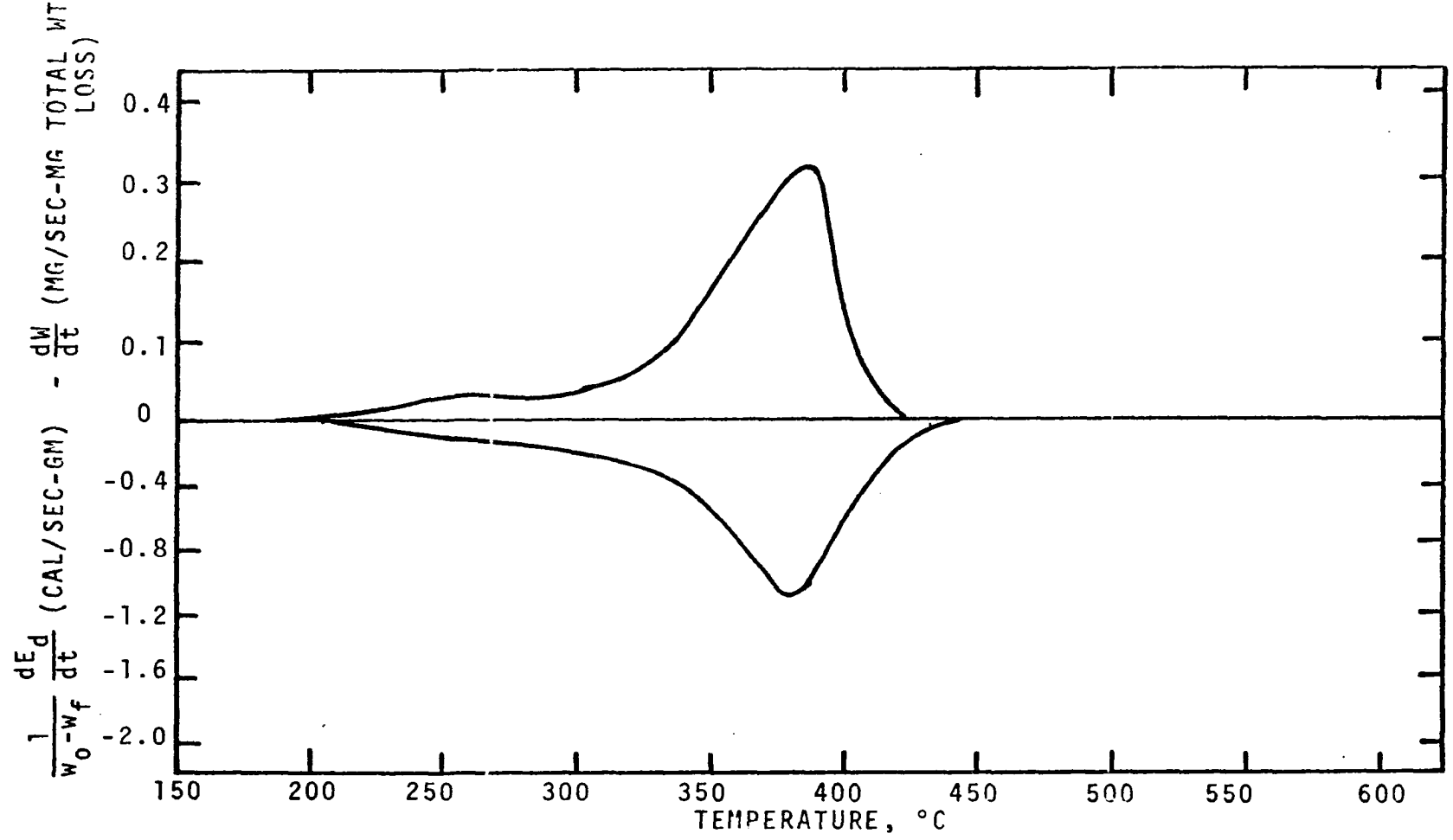

Figure III-43. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 20°C/min.

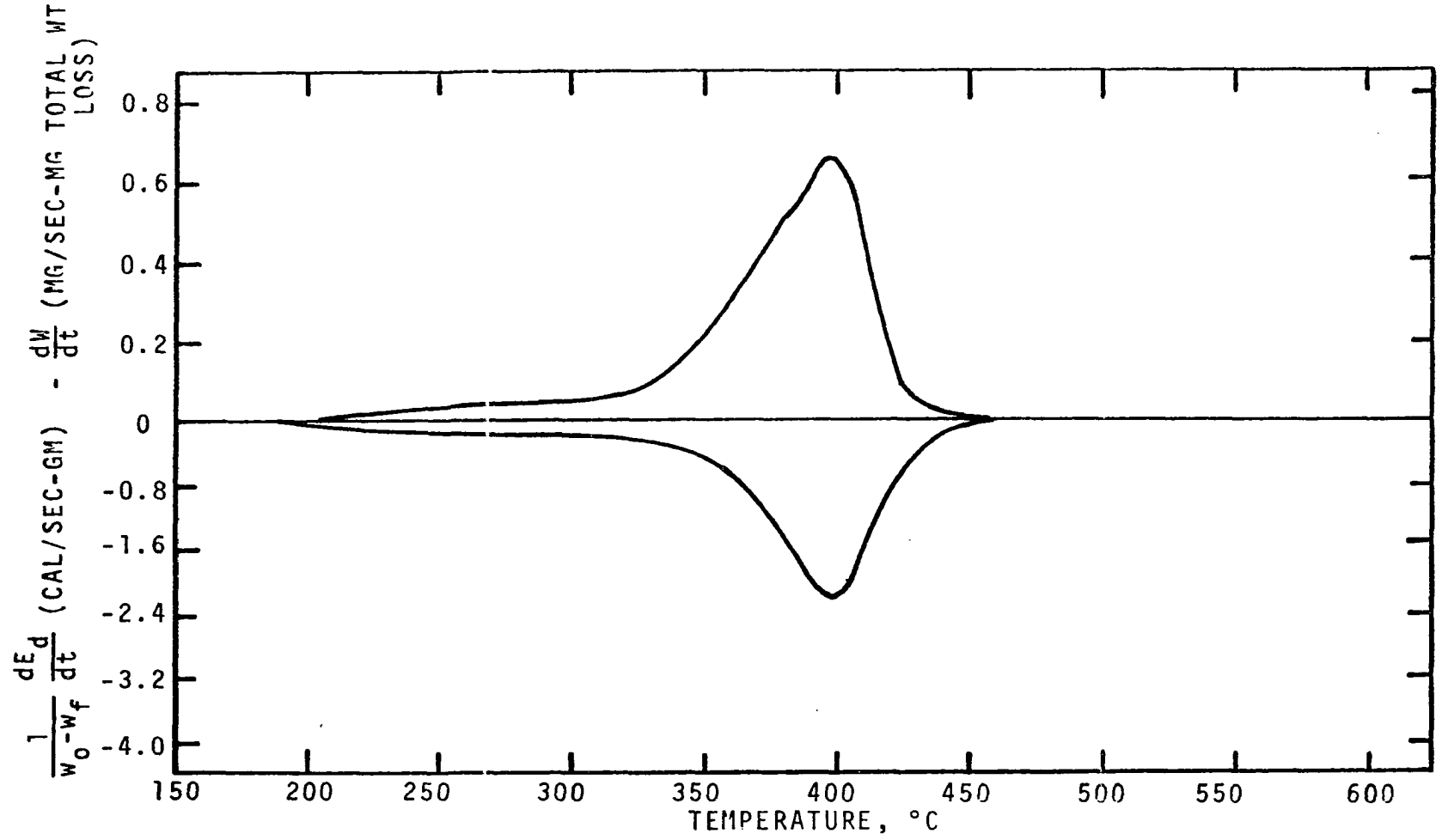

Figure III-44. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Polymethylmethacrylate - Heating Rate, 40°C/min.

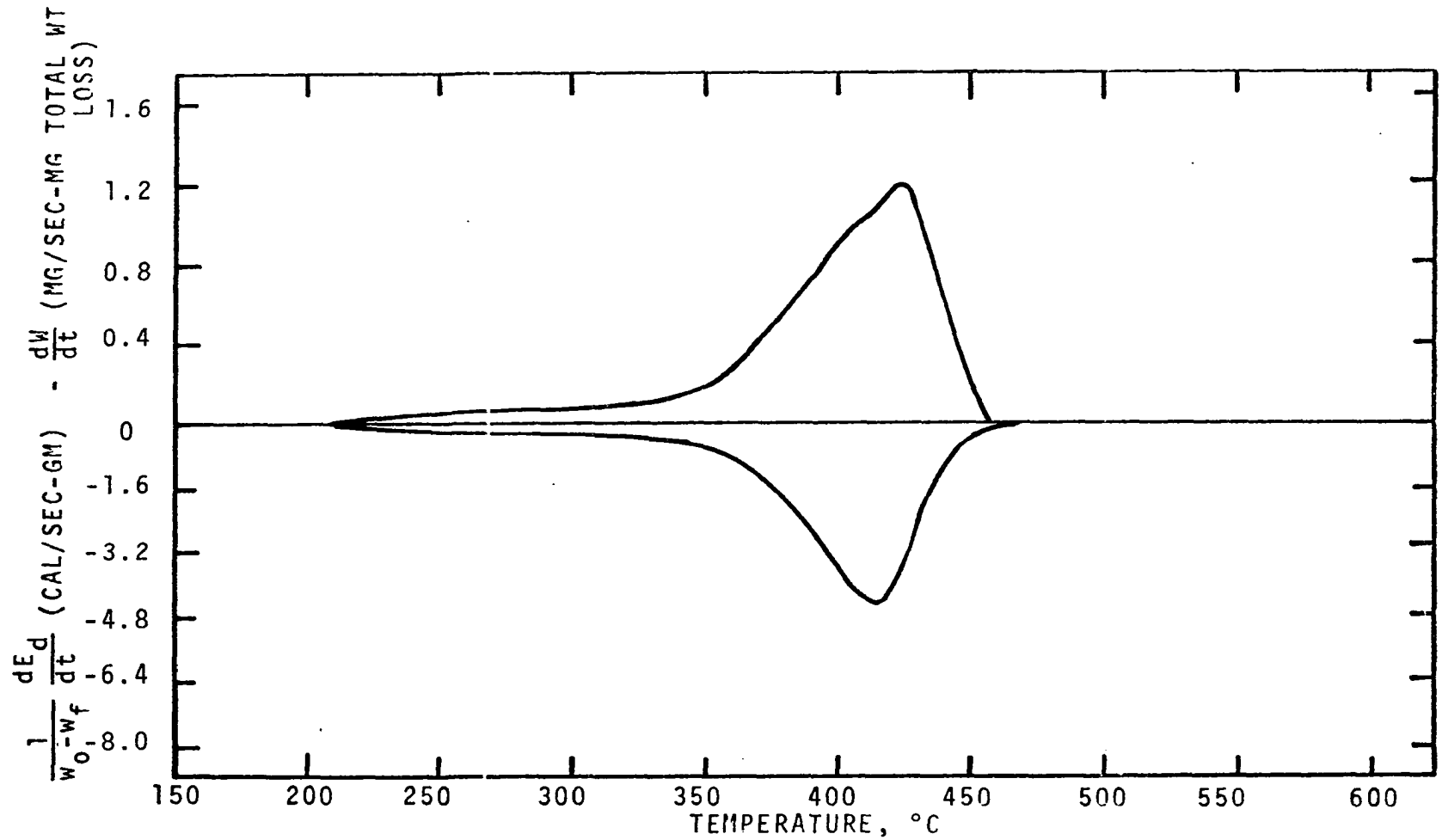

Figure III-45. Comparison of the Rate of Energy Change with the Rate of Weight Loss for Polymethylmethacrylate. Heating Rate - 80°C/min.

CHAPTER IV

ANALYSIS OF POLYMER DECOMPOSITION DATA

In the analysis of the type of kinetic data obtained in this work and presented in the previous chapter, it is important to consider the questions that may be answered and the information that might be obtained from the analysis. These considerations are many times overlooked in studies of this nature. Almost without exception, whenever TGA data are presented, kinetic parameters are calculated for the degradation reaction. Because of the lack of a theoretical connection between the Arrhenius rate equation and polymer decompositions, the significance of these kinetic parameters is obscure. As a very minimum it would seem that parameters obtained from a kinetic analysis should be capable of being using to model the degradation reaction. If the parameters have no real significance, then possibly modeling the degradation is the extent of their usefulness. If, on the other hand, there does turn out to be a theoretical connection between the kinetic parameters and the degradation reaction these parameters must still be capable of reproducing the weight loss characteristics of the decomposition. In reviewing the literature on polymer decomposition only one instance

was found (22) where an author actually used kinetic parameters obtained from experimental data to back calculate weight loss curves. One important contribution that will be sought in this analysis of kinetic data is the specification of kinetic parameters that allow the accurate modeling of the decomposition reaction.

It is impossible, using only the type of decomposition data presented here, to present a detailed, mechanistic description of the degradation reaction. It is possible, using information obtained from a proper kinetic data analysis, to speculate on the number of primary weight loss steps in the degradation. Some of this "educated speculation" will be done later.

Another significant contribution to be presented in this section is the calculation of the energy of decomposition of polystyrene and polymethylmethacrylate. This calculation does not involve any special problems from an analytical standpoint; the major problems are connected with obtaining the experimental data. These data are the first of this type to be presented for synthetic polymers.

Polystyrene Weight Loss Kinetics

The weight loss and rate of weight loss kinetic data obtained for the two polystyrene samples studied were analyzed by two different techniques. In Figures III-7 through III-16 it can be seen that the weight loss curves for polystyrene

decomposition are smooth, and that the rate of weight loss curves exhibit a single peak. Although a rate of weight loss curve with more than one peak indicates that more than one weight loss mechanism is operative, the existence of a single peak does not guarantee a single weight loss step. However, it was felt, because of this single peak, that a single set of kinetic parameters for the equation

$$-\frac{1}{w_o - w_f}\frac{dw}{dt} = Ae^{-E/RT}(W)^n \qquad \text{(IV-1)}$$

might be obtained that would allow the degradation to be accurately modeled.

If the logarithm of both sides of Equation IV-1 is taken, the following is obtained

$$\log\left[-\frac{1}{w_o - w_f}\frac{dw}{dt}\right] = \log A - E/2.3RT + n \log W \qquad \text{(IV-2)}$$

Rearranging this equation slightly gives

$$\log\left[-\frac{1}{w_o - w_f}\frac{dw}{dt}\right] - n \log W = \log A - E/2.3RT \qquad \text{(IV-3)}$$

Now, if indeed a single set of parameters may be obtained over the entire decomposition range, the "best" value of n may be defined as the one which gives the best straight line when the left side of Equation IV-3 is plotted versus 1/T. Log A may be obtained from the intercept of this straight line and E calculated from the slope. A one-dimensional

search over n was made, at each heating rate, for the two polystyrene samples. The results of this optimization are given in Table IV-1. A plot of the left side of Equation IV-3 versus $1/T$ is shown in Figure IV-1 for clear polystyrene at a heating rate of 40°C/min. A similar plot for white polystyrene is given in Figure IV-2.

As can be seen from Table IV-1 there is some variation in kinetic parameters with heating rate. The next step was to investigate the possibility of obtaining a single set of parameters that would apply at all heating rates, for each of the two polystyrene samples. A plot was made of log A versus E for each of the two samples. These plots are shown in Figures IV-3 and IV-4. Only the values of log A and E corresponding to the best value of n are plotted in Figures IV-3 and IV-4. At each heating rate, during the search for the best value of n, a series of n's and their corresponding values of log A and E were obtained. It was found that <u>all</u> of these corresponding log A and E values fit on the same straight lines shown in these two figures. Using this observation a second search was made to obtain a single set of parameters that best fit the data over all heating rates. This search was a two-dimensional one with one parameter being n and the second being the straight line given in the log A versus E plot. The parameters obtained, that apply over all heating rates studied, are given in Table IV-2 for each of the polystyrene samples.

TABLE IV-1

OPTIMIZED KINETIC PARAMETERS FROM EQUATION IV-3
FOR POLYSTYRENE DECOMPOSITION

	Heating Rate (°C/min)	log A (1/sec)	E (cal/mole)	n
Clear Polystyrene	10	18.17	57,908.	0.87
	20	22.07	70,247.	0.97
	40	20.36	65,829.	0.83
	80	16.74	54,904.	0.67
	160	14.84	48,612.	0.64
White Polystyrene	10	8.04	27,579.	0.64
	20	9.72	32,602.	0.70
	40	9.75	32,651.	0.59
	80	11.05	36,622.	0.61
	160	12.99	43,055.	0.72

TABLE IV-2

KINETIC PARAMETERS THAT APPLY AT ALL HEATING RATES
STUDIED FOR POLYSTYRENE DECOMPOSITION

	log A	E	n
Clear Polystyrene	14.09	54,834.	0.50
White Polystyrene	12.72	42,101.	0.90

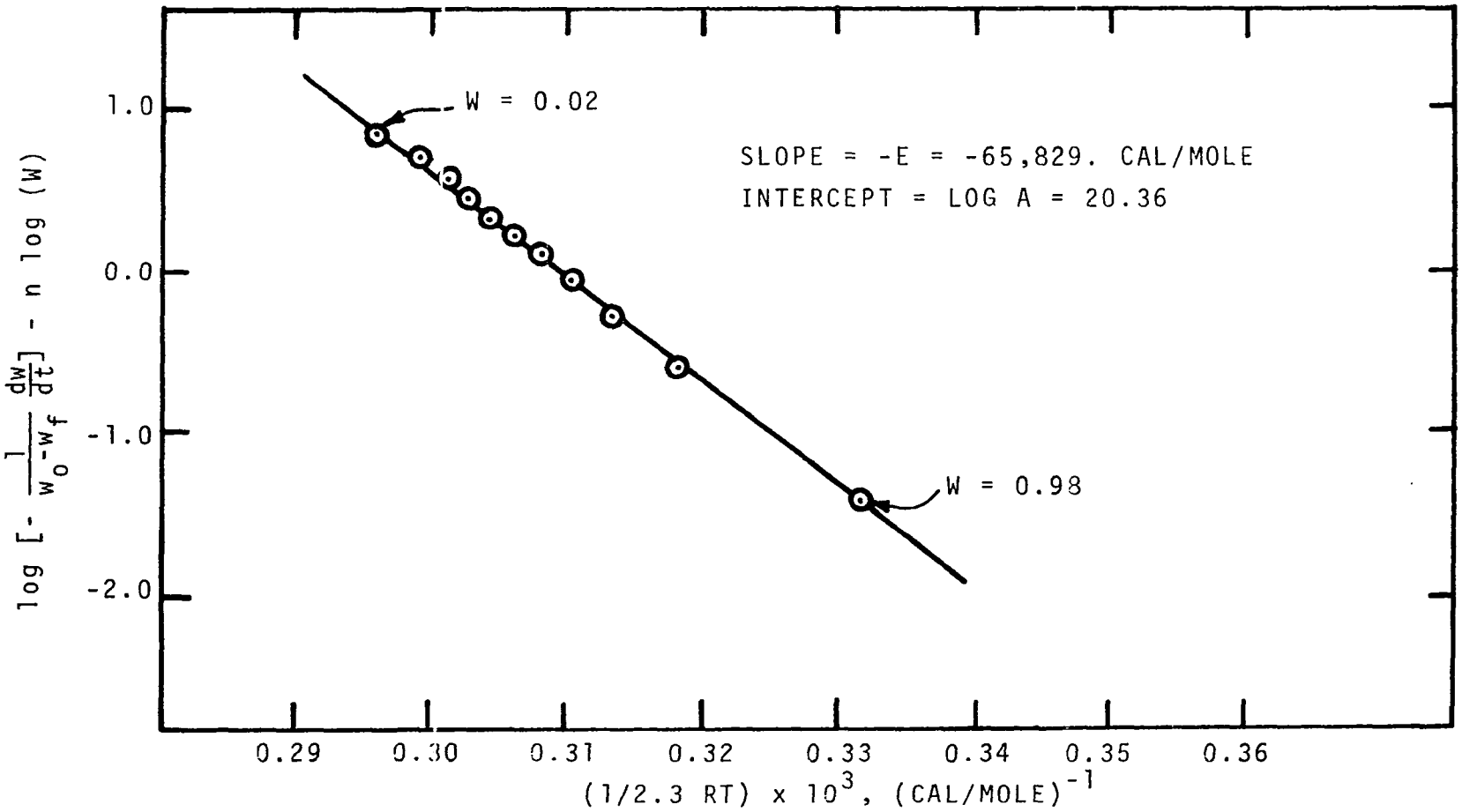

Figure IV-1. Best Straight Line According to Equation IV-3 for Clear Polystyrene. n = 0.83. Heating Rate ~ 40°C/min.

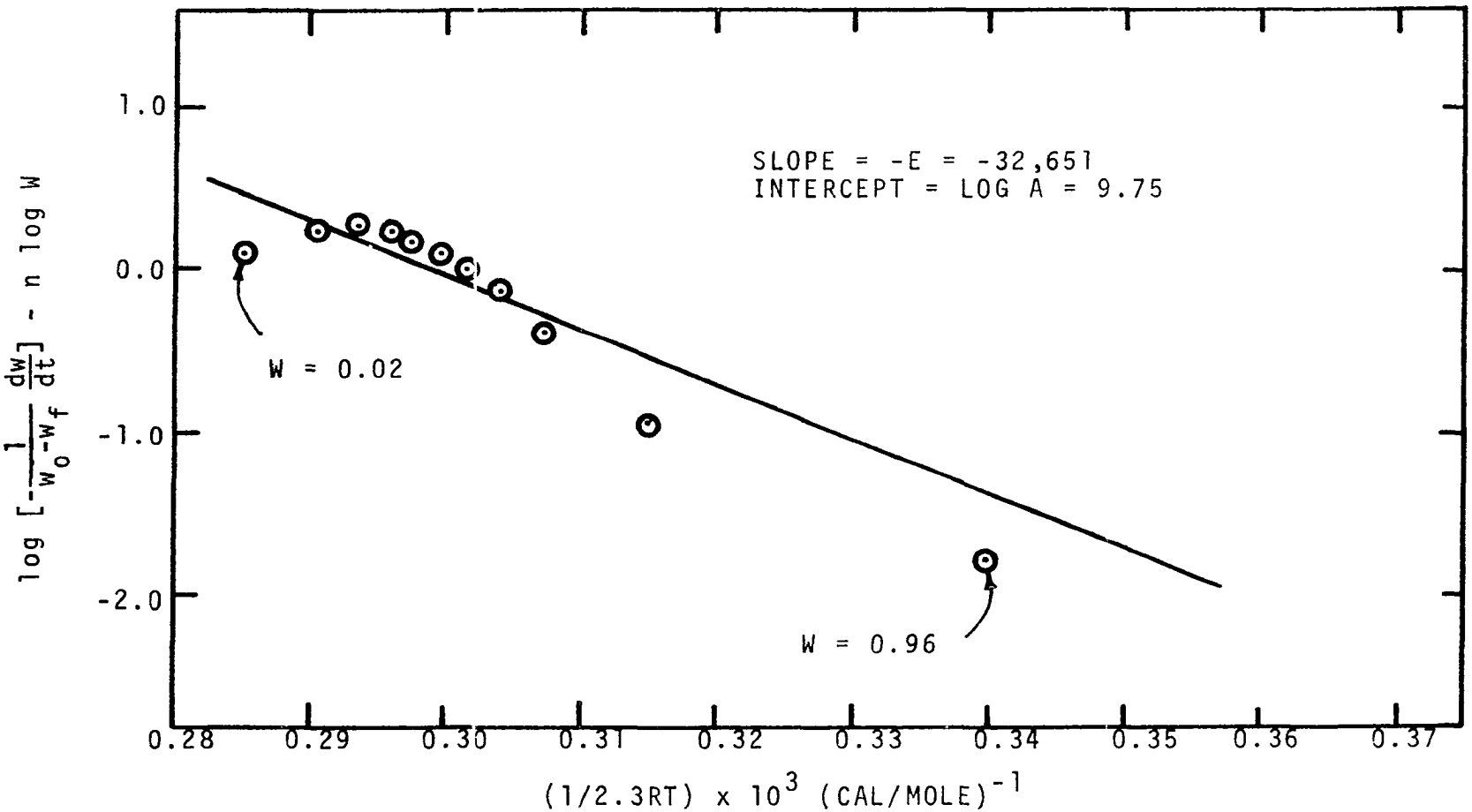

Figure IV-2. Best Straight Line According to Equation IV-3 for White Polystyrene. n = 0.59. Heating Rate - 40°C/min.

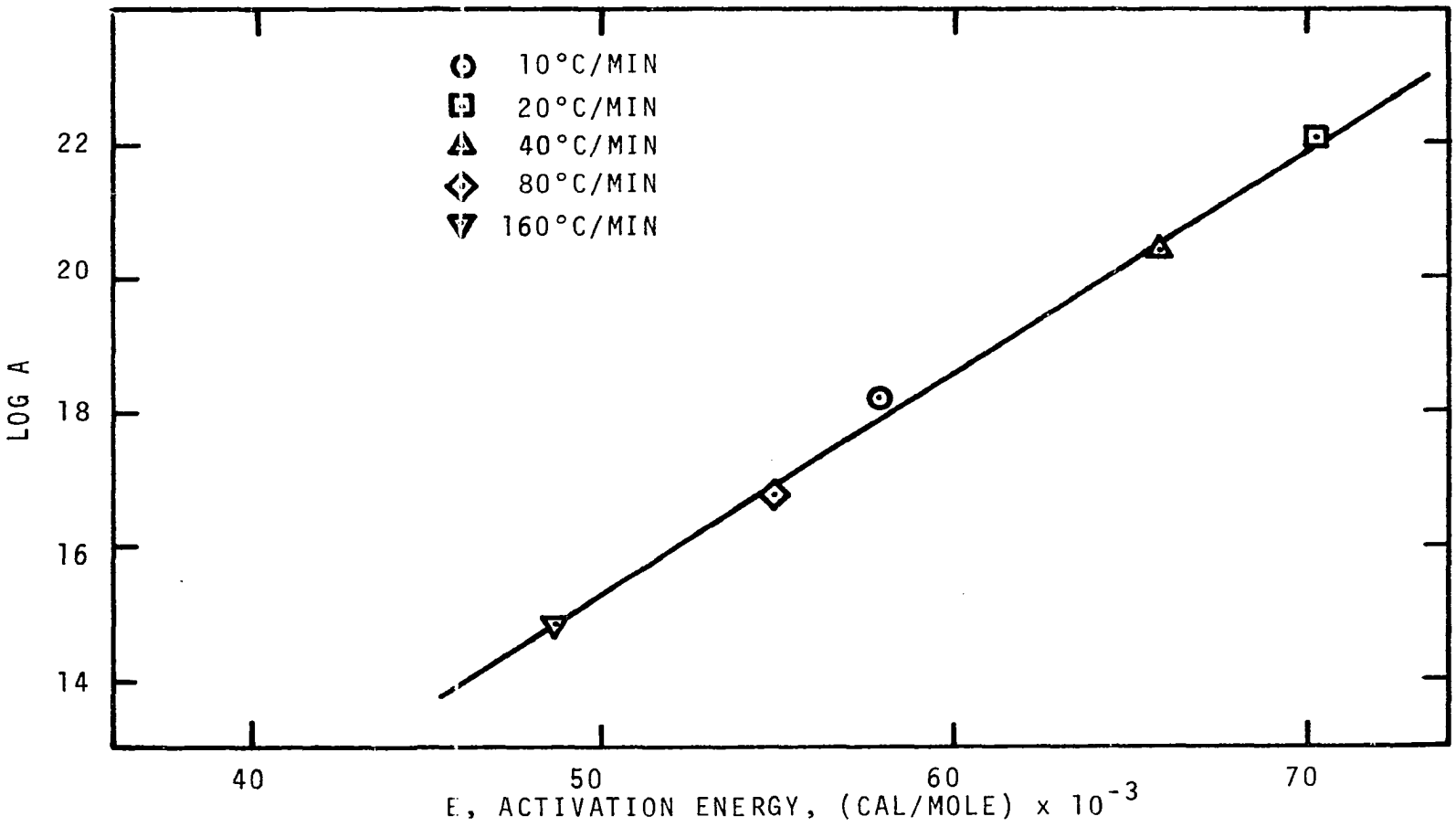

Figure IV-3. Relationship Between E and Log A for Clear Polystyrene.

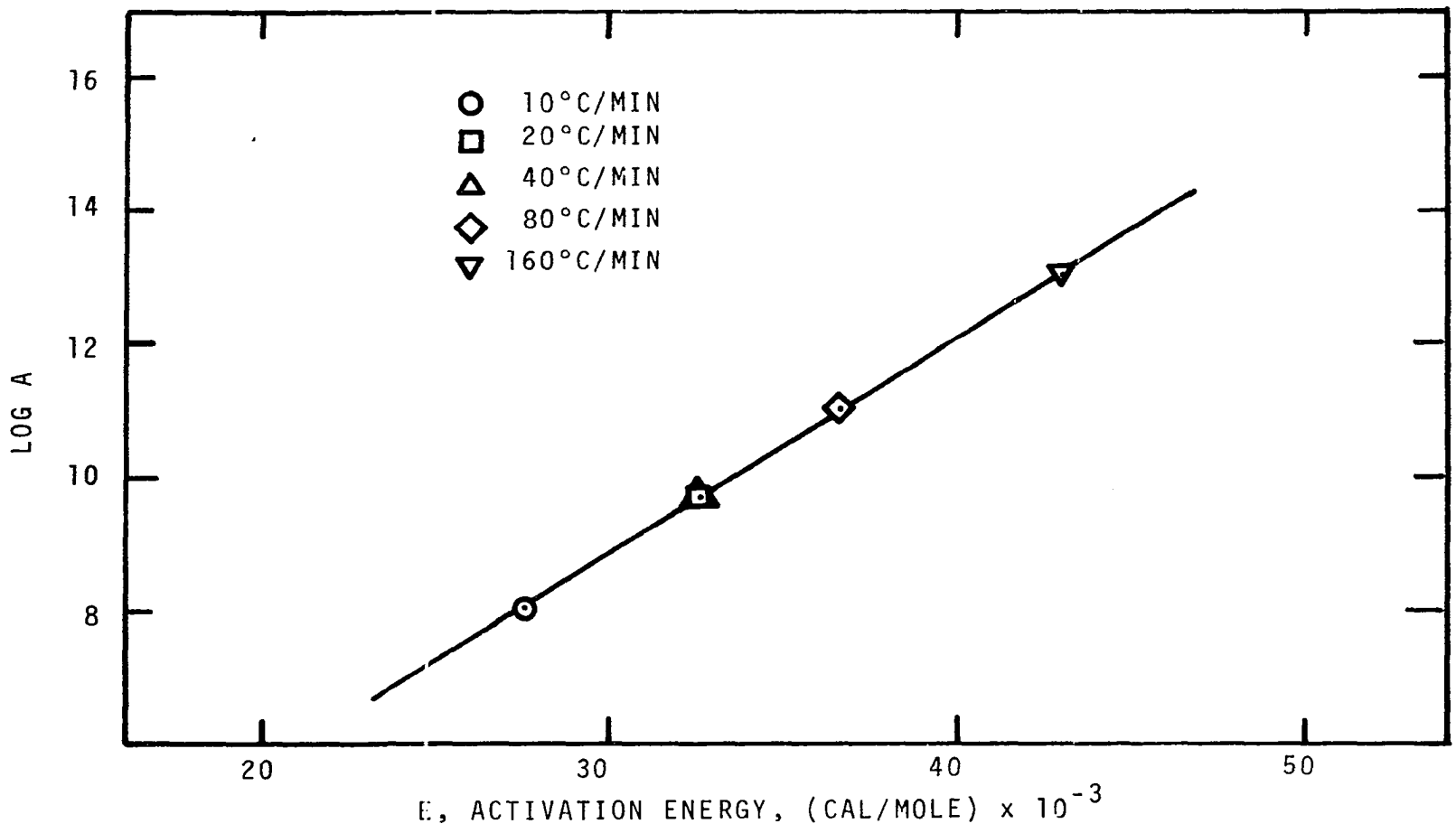

Figure IV-4. Relationship Between E and Log A for White Polystyrene.

In order to evaluate the ability of the kinetic parameters to model the degradation reaction, it is necessary to back calculate the weight loss curves using these parameters. To accomplish this Equation IV-1 is given in integral form.

$$-\frac{1}{w_o - w_f}\int_{w_o}^{w}\frac{dw}{[(w-w_f)/(w_o-w_f)]^n} = A\int_{T_o}^{T} e^{-E/RT}dt \qquad \text{(IV-4)}$$

The heating rate, β, is given by

$$T = T_o + \beta t \qquad \text{(IV-5)}$$

where T_o is the initial temperature and

$$dT = \beta\, dt \qquad \text{(IV-6)}$$

Substituting Equation IV-6 into IV-4 gives

$$-\frac{1}{w_o - w_f}\int_{w_o}^{w}\frac{dw}{[(w-w_f)/(w_o-w_f)]^n} = A/\beta\int_{T_o}^{T} e^{-E/RT}\, dT \qquad \text{(IV-7)}$$

Integrating the left side of Equation IV-7 obtains for $n \neq 1$

$$(1-n)\left[1 - \left(\frac{w-w_f}{w_o - w_f}\right)^{1-n}\right] = A/\beta\int_{T_o}^{T} e^{-E/RT}\, dT \qquad \text{(IV-8)}$$

The exponential integral in Equation IV-8 requires numerical integration. By performing this integration at each heating rate the weight loss curves may be obtained. Knowing the weight loss as a function of temperature, the rate of weight loss may be calculated directly from Equation IV-1. In

Figures IV-5 and IV-6 the experimental weight loss curves and the calculated weight loss, using the "best" kinetic parameters from Table IV-1, are compared for the two polystyrenes. Only the 10°C/min and the 160°C/min curves are shown to preserve clarity. Figures IV-7 and IV-8 compare the curves using the single set of parameters given in Table IV-2. It would be expected that the calculated curves, using the "best" parameters, would give a slightly better fit to the experimental data. However, the calculated curves from the single set of parameters in most instances fit the data within experimental error. Thus the single set of parameters is equally as valid as the "best" parameters.

One interesting fact was observed during this data analysis in connection with Figures IV-3 and IV-4. The slope and intercept of the straight line in Figure IV-3 are 0.327×10^{-3} and -0.90, respectively. For the straight line in Figure IV-4, the slope is 0.322×10^{-3} and the intercept -0.82. These values indicate that the points in Figures IV-3 and IV-4, from two different polystyrene samples, define essentially a single straight line. A definite explanation for this phenomenon cannot be given at this time. The possibility exists that this line is characteristic of polystyrene decomposition in general, regardless of the polystyrene formulation under consideration. Additional data on other polystyrene samples would be required to test this possibility.

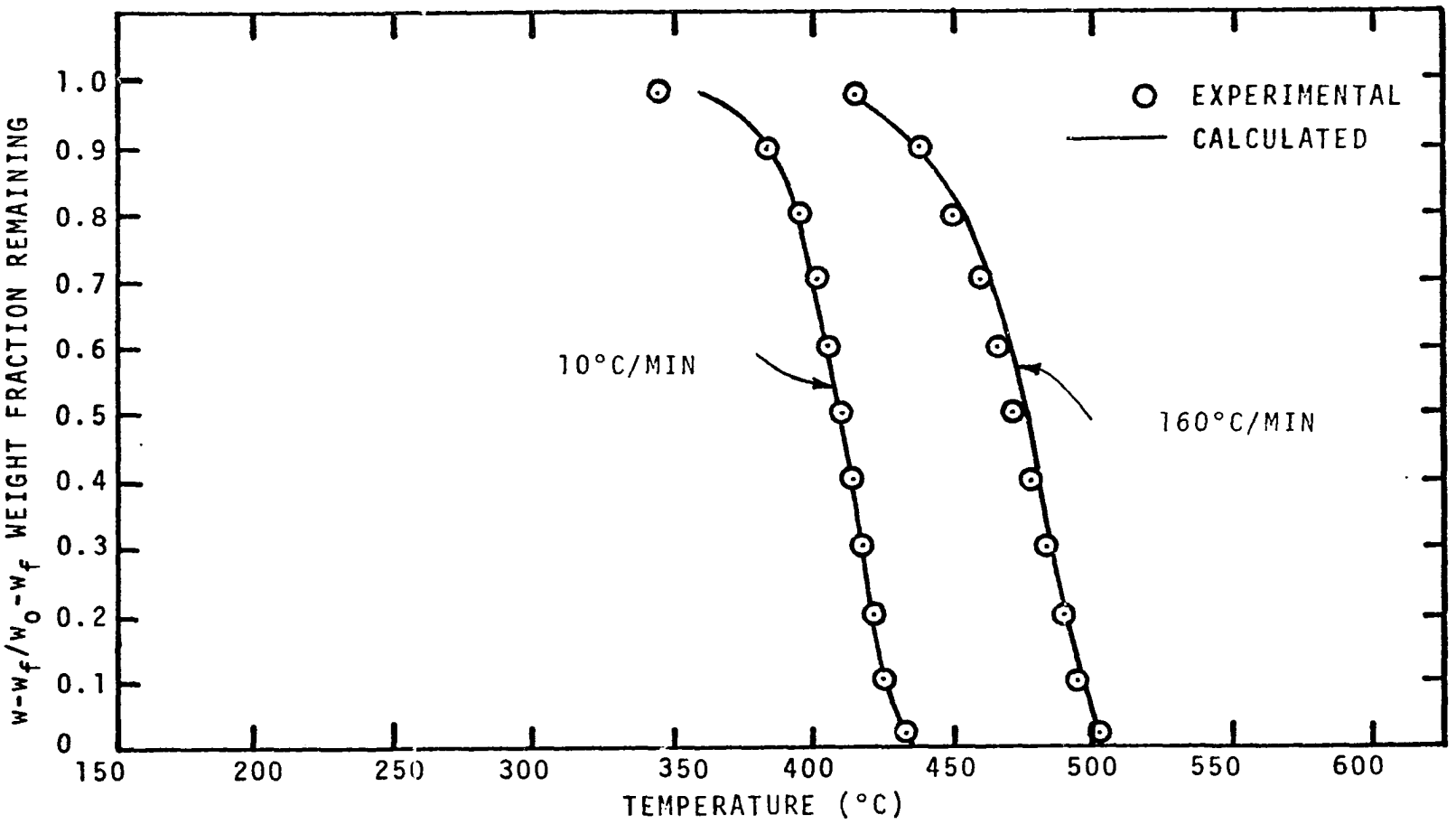

Figure IV-5. Comparison of Experimental and Calculated Weight Loss Curves for Clear Polystyrene Using "Best" Parameters.

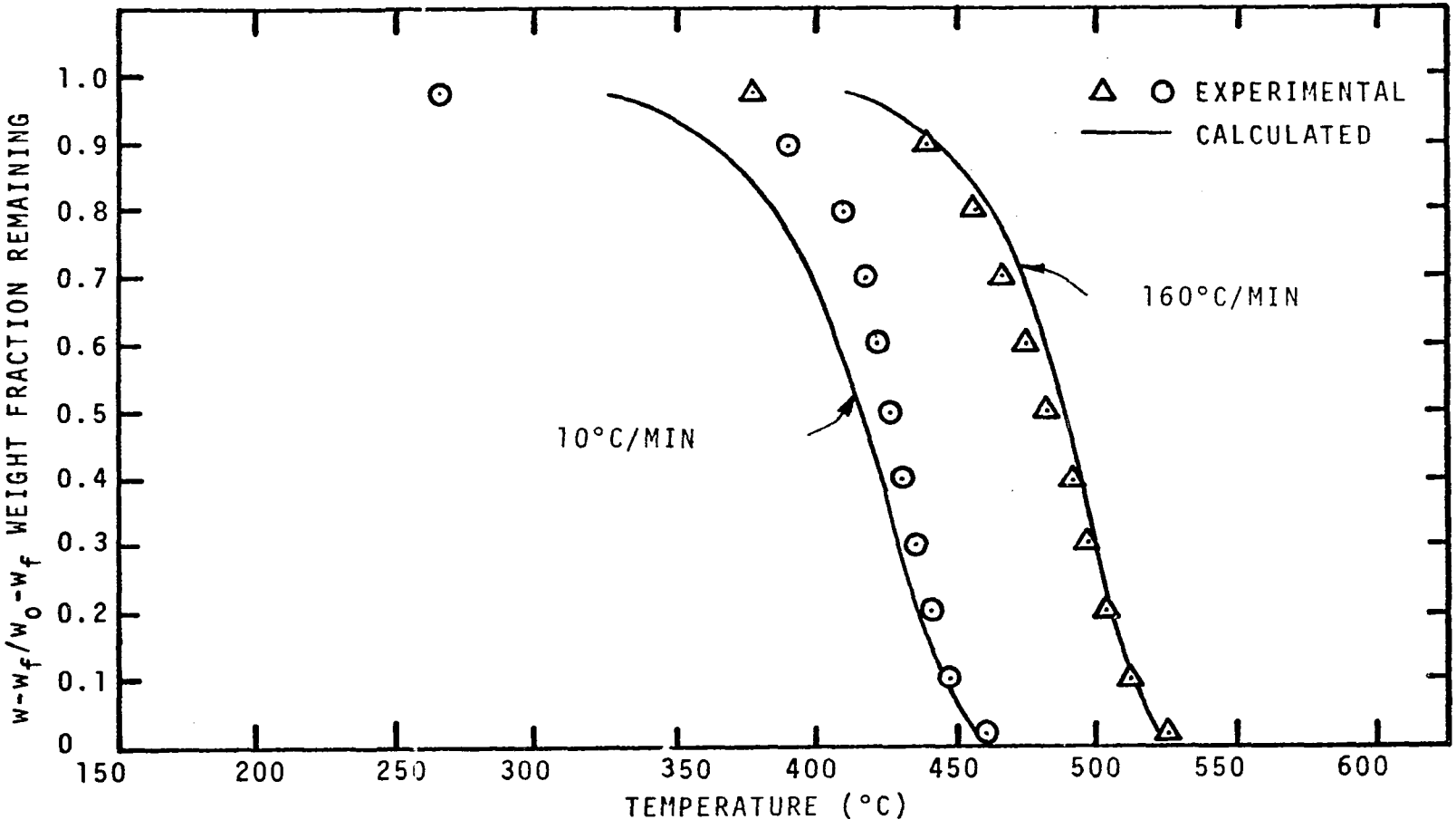

Figure IV-6. Comparison of Experimental and Calculated Weight Loss Curves for White Polystyrene Using "Best" Parameters.

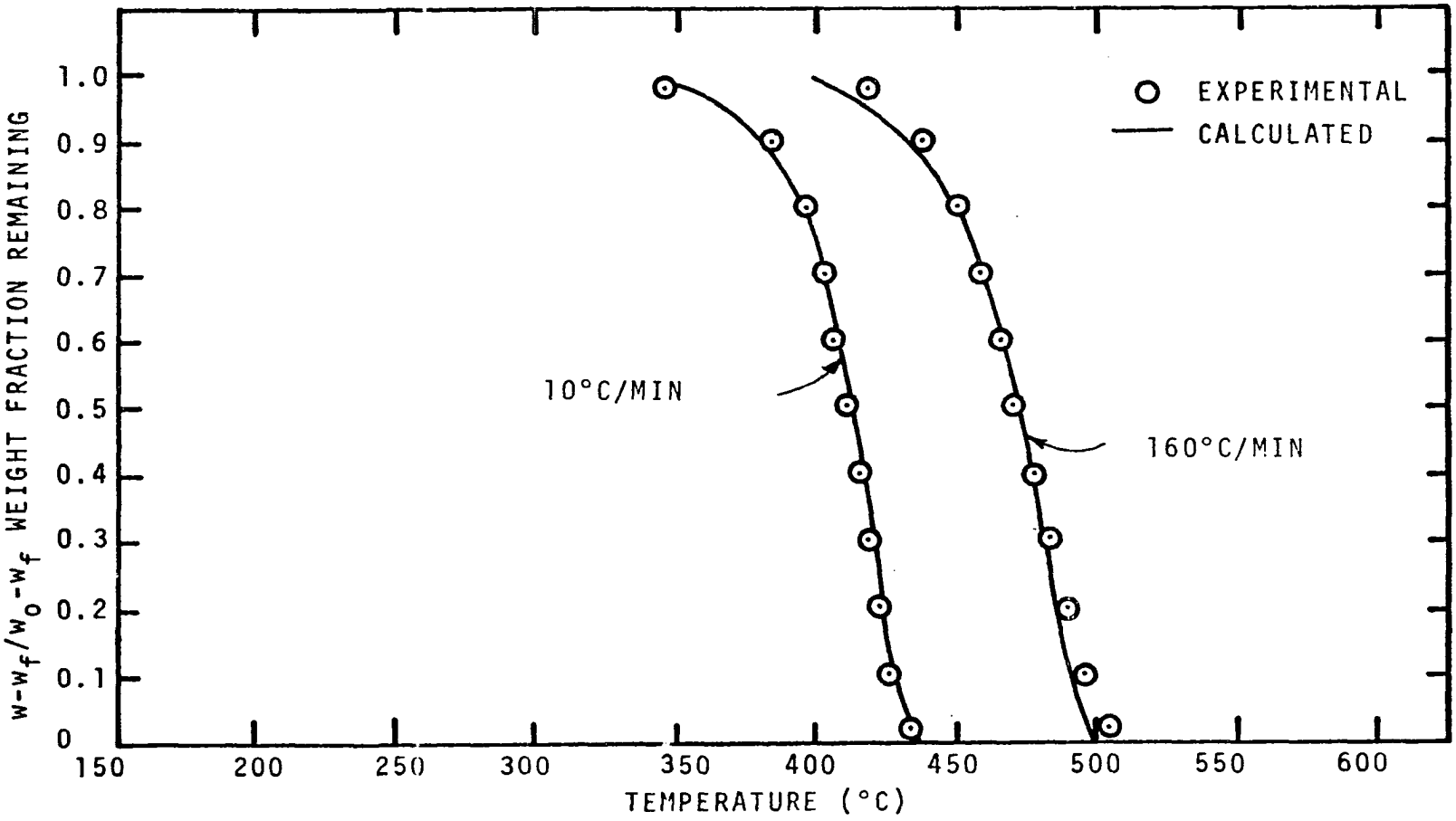

Figure IV-7. Comparison of Experimental and Calculated Weight Loss Curves for Clear Polystyrene Using a Single Set of Parameters.

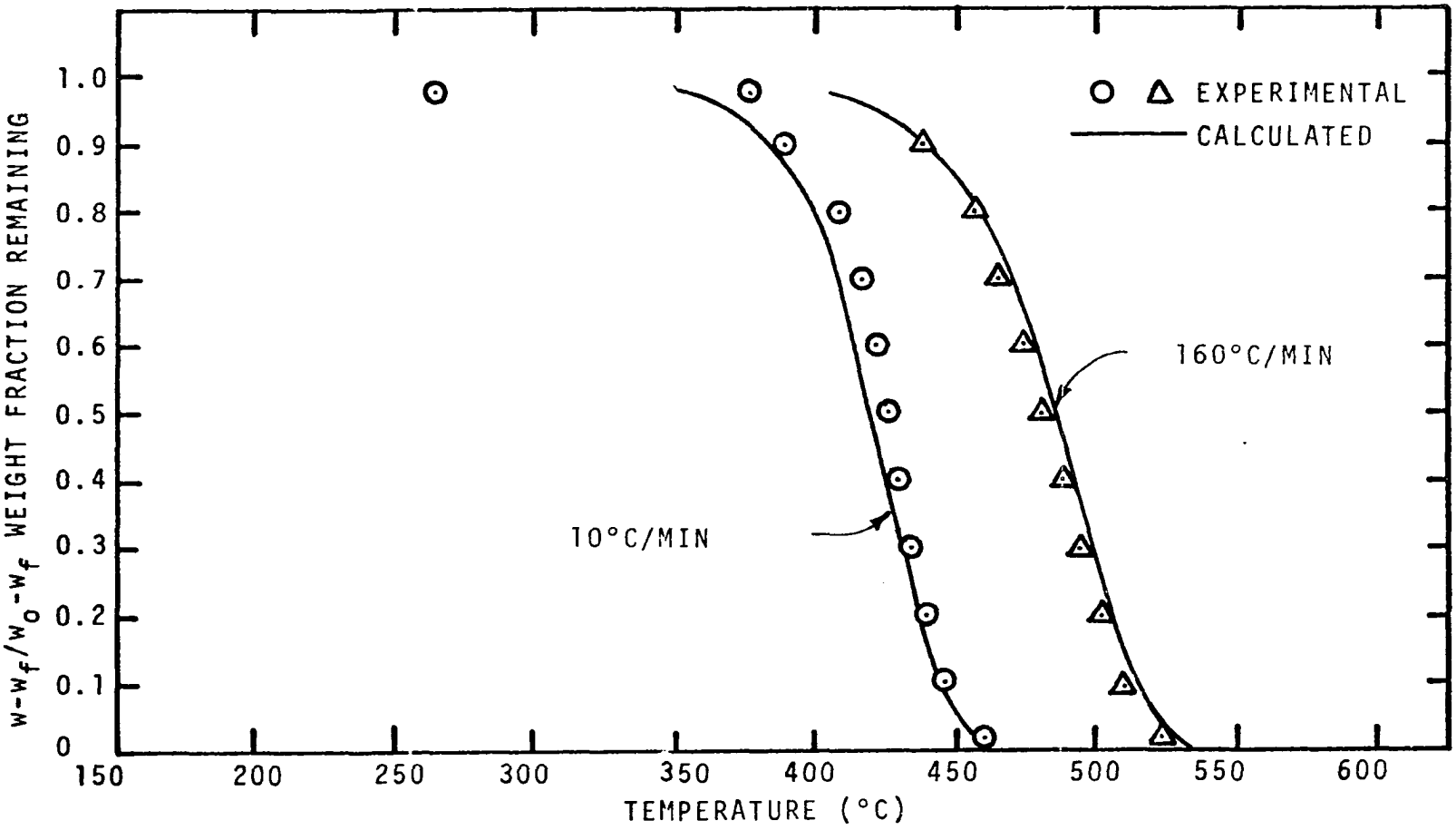

Figure IV-8. Comparison of Experimental and Calculated Weight Loss Curves for White Polystyrene Using a Single Set of Parameters.

The second method of kinetic data analysis applied to the polystyrene decomposition data is that of Friedman (29). This technique is described in detail in Chapter II and only the equations used will be presented here. This technique requires data at several heating rates and uses the equation

$$\log \left[-\frac{1}{w_o - w_f} \frac{dw}{dt}\right]_\beta = \log [Af(W)] - E/2.3RT_\beta \qquad \text{(IV-9)}$$

where the β subscript indicates that the rate and temperature corresponding to any specific value of conversion, W, depend upon heating rate. At various values of conversion throughout the degradation range, values of $\log [-1/(w_o-w_f) \cdot dw/dt]_\beta$ and T_β are obtained. A plot of $\log [-1/(w_o-w_f) \cdot dw/dt]_\beta$ versus $1/T_\beta$ is made. The activation energy may be obtained from the slope of the line and log [Af(W)] from the intercept, for each value of conversion. An example of this type of plot is shown in Figure IV-9. The variation in activation energy with conversion may be examined for the two polystyrene samples in Figures IV-10 and IV-11. Average values of activation energy are then calculated over the entire degradation range. For clear polystyrene the average E is 39,075. cal/mole and for white polystyrene the average is 45,797 cal/mole. The average activation energy is then used to calculate log [Af(W)] values at each conversion. Plots of log [Af(W)] versus log W are shown in Figures IV-12 and IV-13. Goldfarb (30) states that this type of plot will reveal the rate law for the decomposition. Figures IV-12 and IV-13 have the same general

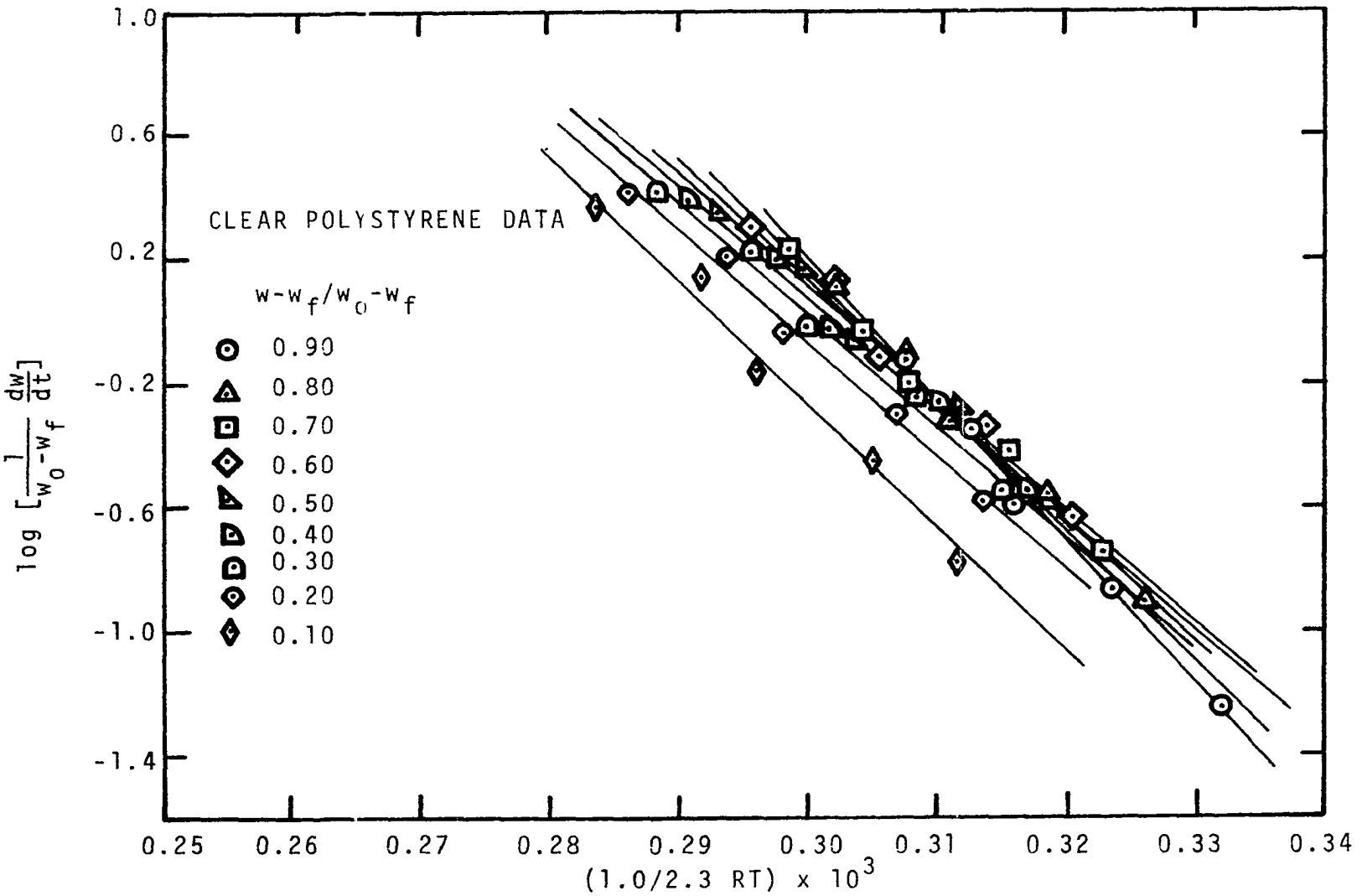

Figure IV-9. Plot to Obtain Activation Energy at Various Values of Conversion. Method of Friedman.

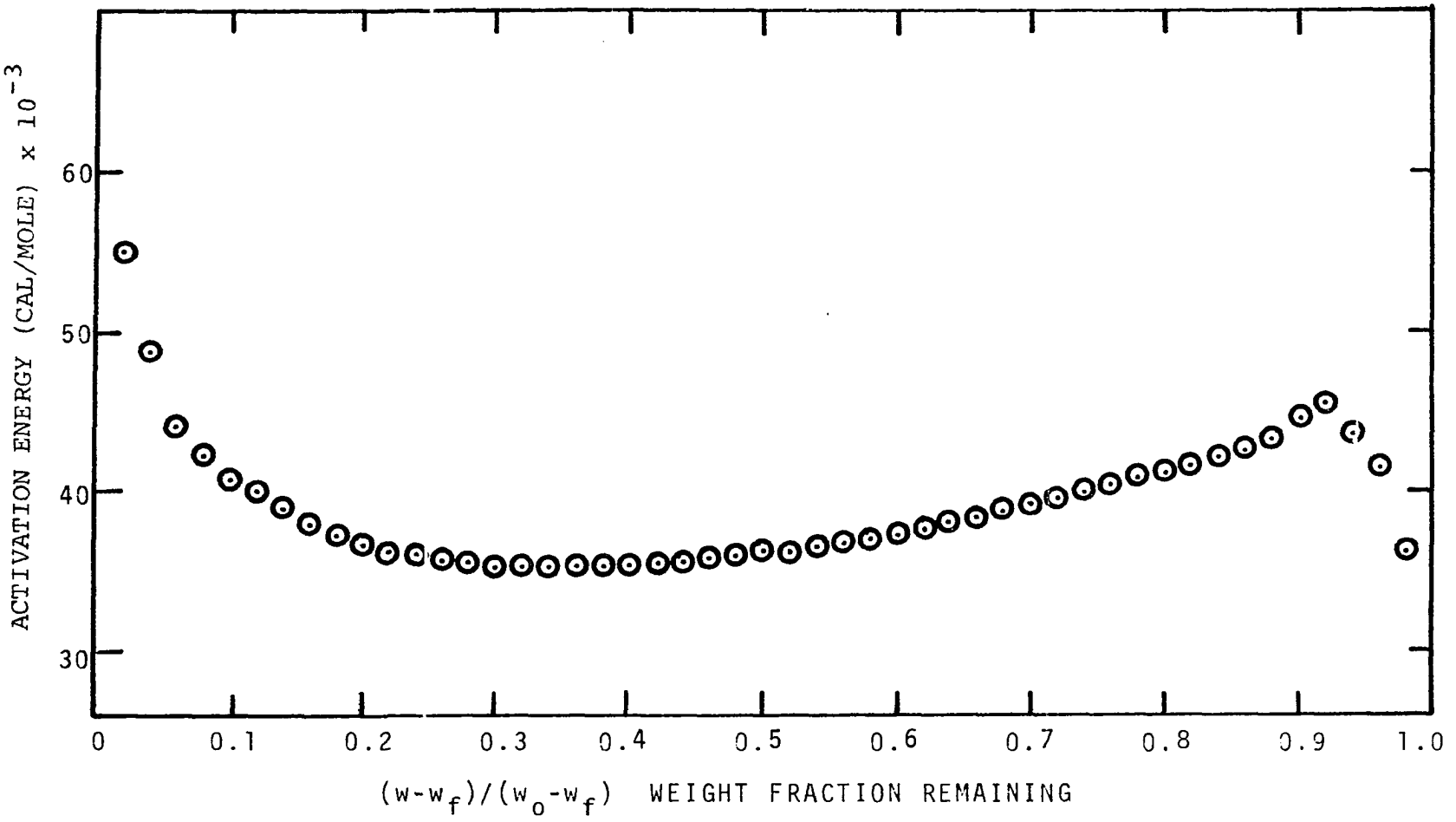

Figure IV-10. Variation of Activation Energy with Conversion for Clear Polystyrene. Method of Friedman.

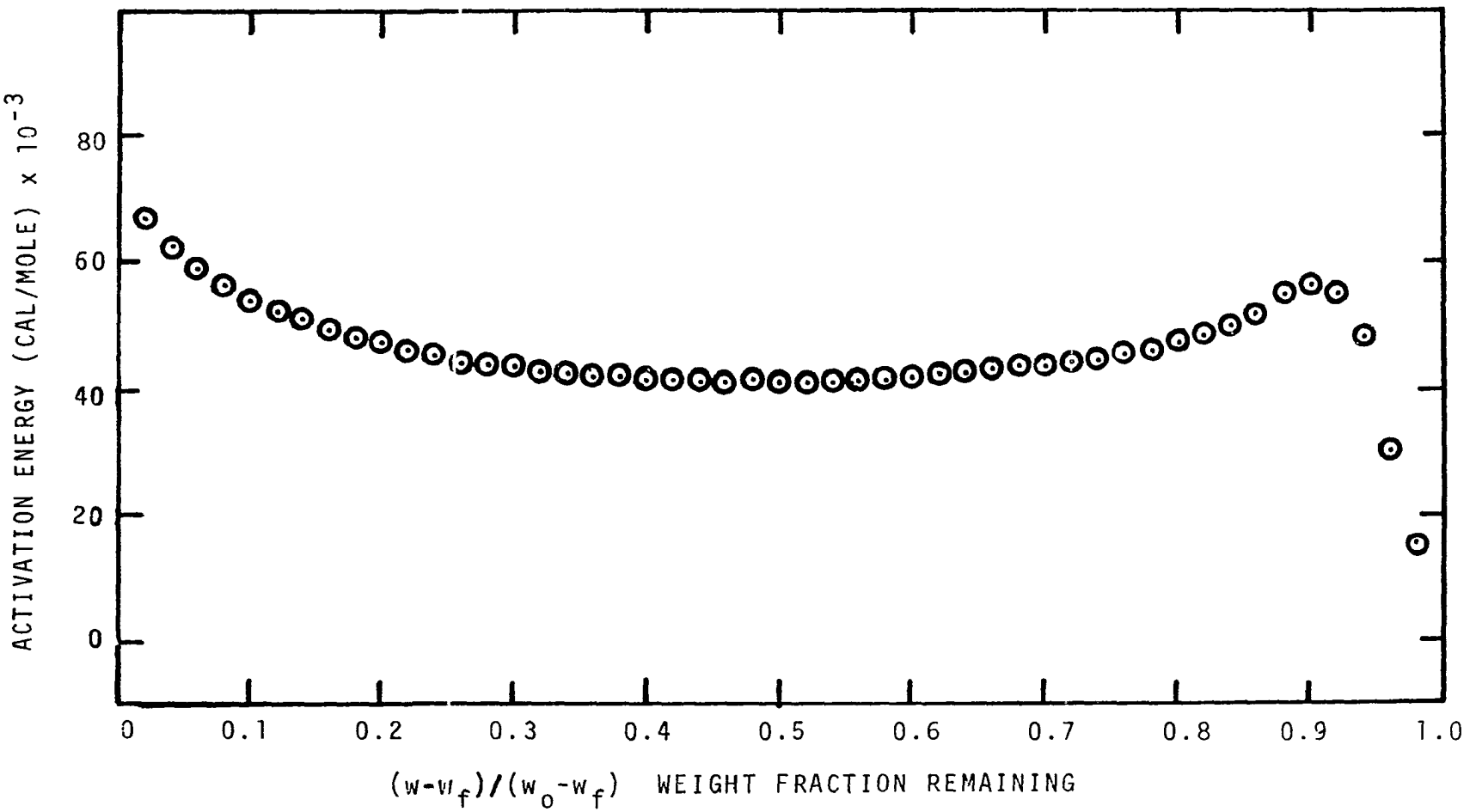

Figure IV-11. Variation of Activation Energy with Conversion for White Polystyrene. Method of Friedman.

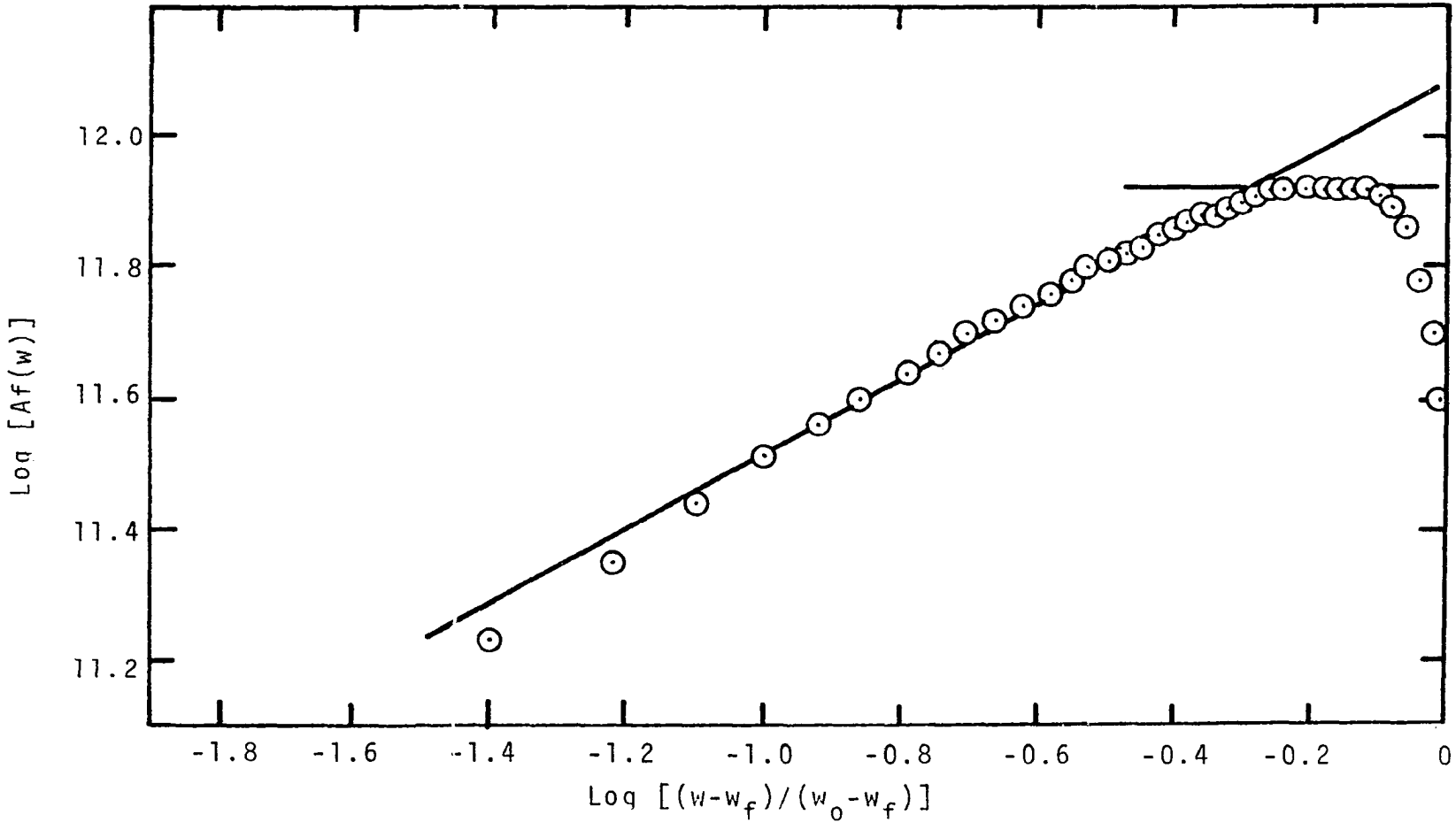

Figure IV-12. Plot of Log [Af(w)] versus W for Clear Polystyrene. Method of Friedman.

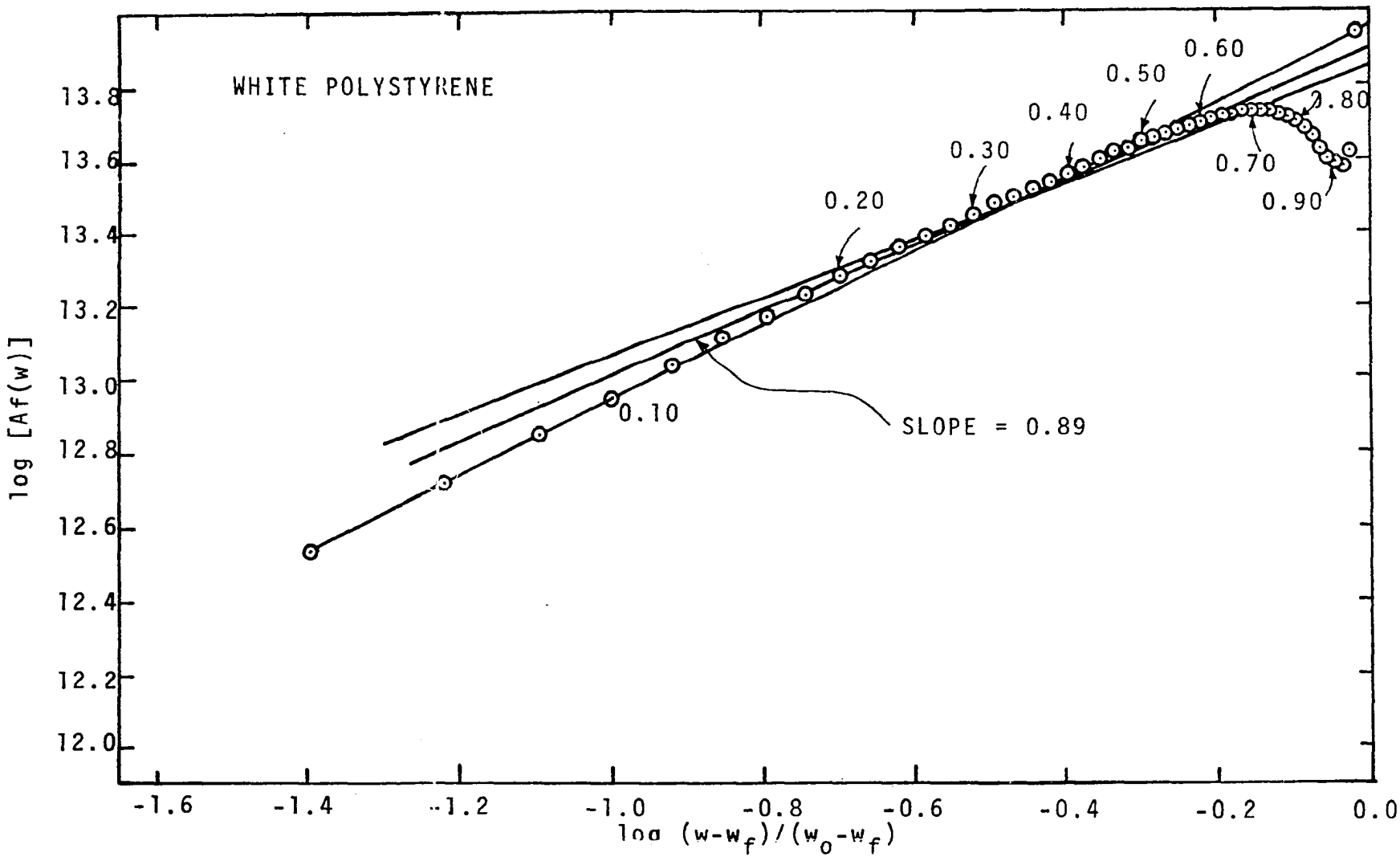

Figure IV-13. Plot of Log [Af(w)] Against Log W for White Polystyrene. Method of Friedman.

characteristics. The initial period of degradation, up to approximately 50 percent weight loss, is indicated to be of zero order for both samples. From 50 percent to 100 percent weight loss the clear polystyrene sample has an indicated order of 0.58 while the white polystyrene has an indicated order of 0.89.

The previous discussion is the standard interpretation of experimental data according to the Friedman method of analysis. Other interpretations are possible. In Flynn and Wall's (28) review of the Friedman technique, covered in Chapter II, interpretation of the analytical results was simplified because the reaction kinetics were known and the technique was applied to calculated data. In the practical application of this technique, the analytical results are much less clear, as will be shown.

Using the average activation energy to calculate log [Af(W)] values implies the assumption of a constant activation energy with fluctuations due to experimental error or an imperfect match of the model to the process. The calculated curves for clear polystyrene shown in Figure IV-7 using the single set of kinetic parameters, certainly fit the experimental data within experimental accuracy. It is assumed for the moment that this set of kinetic parameters gives the true representation of the decomposition of this particular polystyrene sample. The weight loss and rate of weight loss curves calculated from the equation

$$-\frac{1}{w_o - w_f}\frac{dw}{dT} = [10^{14.09}/\beta]\, e^{-54,834/RT}(W)^{0.5} \qquad \text{(IV-10)}$$

then represent the actual degradation kinetics of this clear polystyrene sample. If Friedman's method of analysis is applied to the calculated clear polystyrene data, a constant activation energy of 54,800 cal/mole is obtained over the entire degradation range. The log [Af(W)] versus log W plot gives a straight line of slope 0.5 and intercept of 14.09. In other words, this technique will give back exactly the same parameters used to calculate the data. Thus, the possibility exists that small experimental errors may cause Friedman's technique to give completely erroneous results.

In applying this technique the log [Af(W)] values may be calculated just as readily with the individual values of activation energy as with the average E. If the changes in activation energy shown in Figures IV-10 and IV-11 are real, and therefore not due to experimental error, it would only seem logical to use the individual activation energy values. This calculation was done for white polystyrene, and the curve shown in Figure IV-14 was obtained. The fact that approximately the last 50 percent of the decomposition shows a negative reaction order makes this curve meaningless.

The log [Af(W)] values calculated from the individual activation energies are shown in Figures IV-15 and IV-16 plotted against these activation energies for the two polystyrene

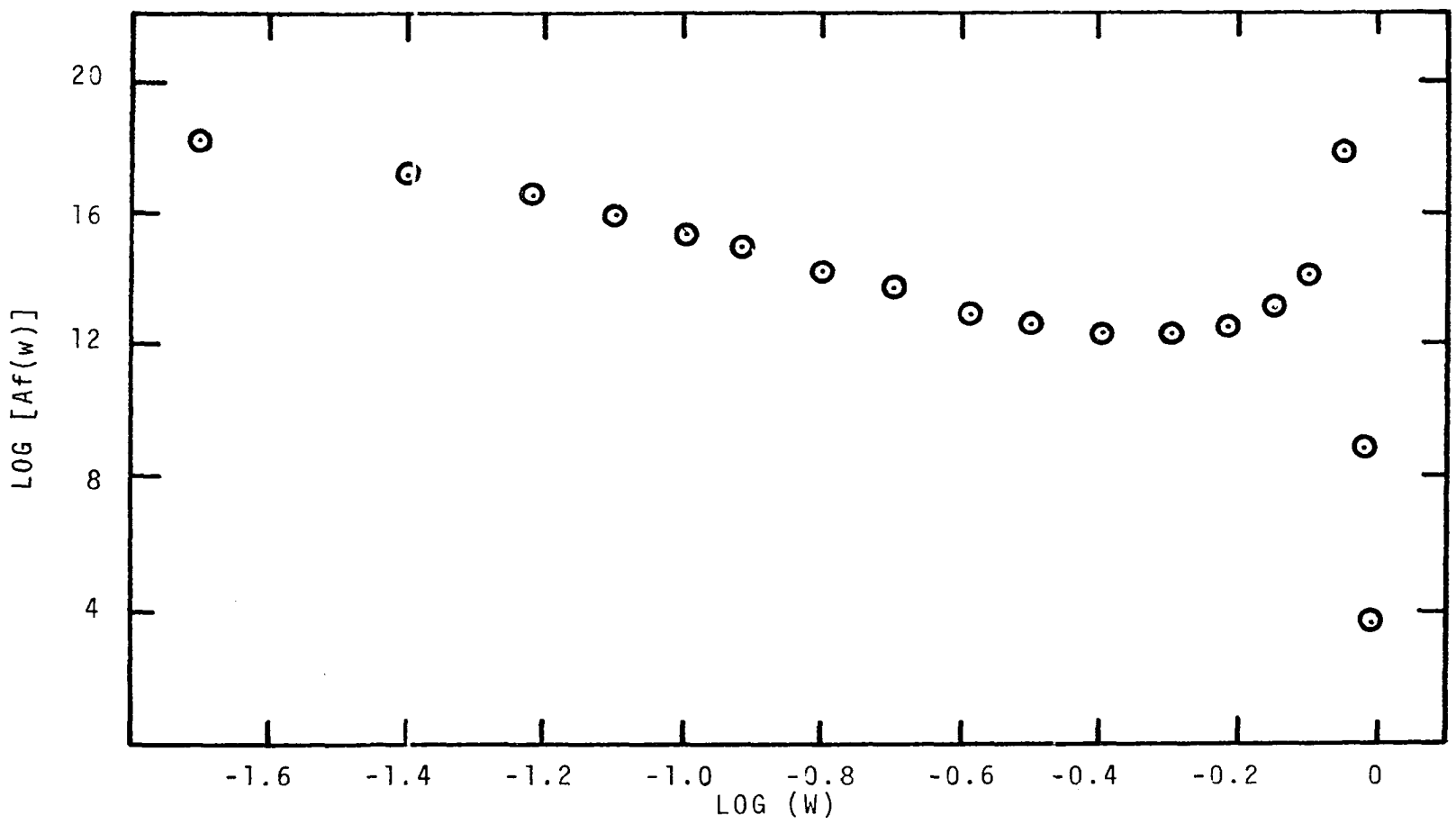

Figure IV-14. Plot of Log [Af(w)] Calculated From Individual Activation Energies Against Log (w). Method of Friedman.

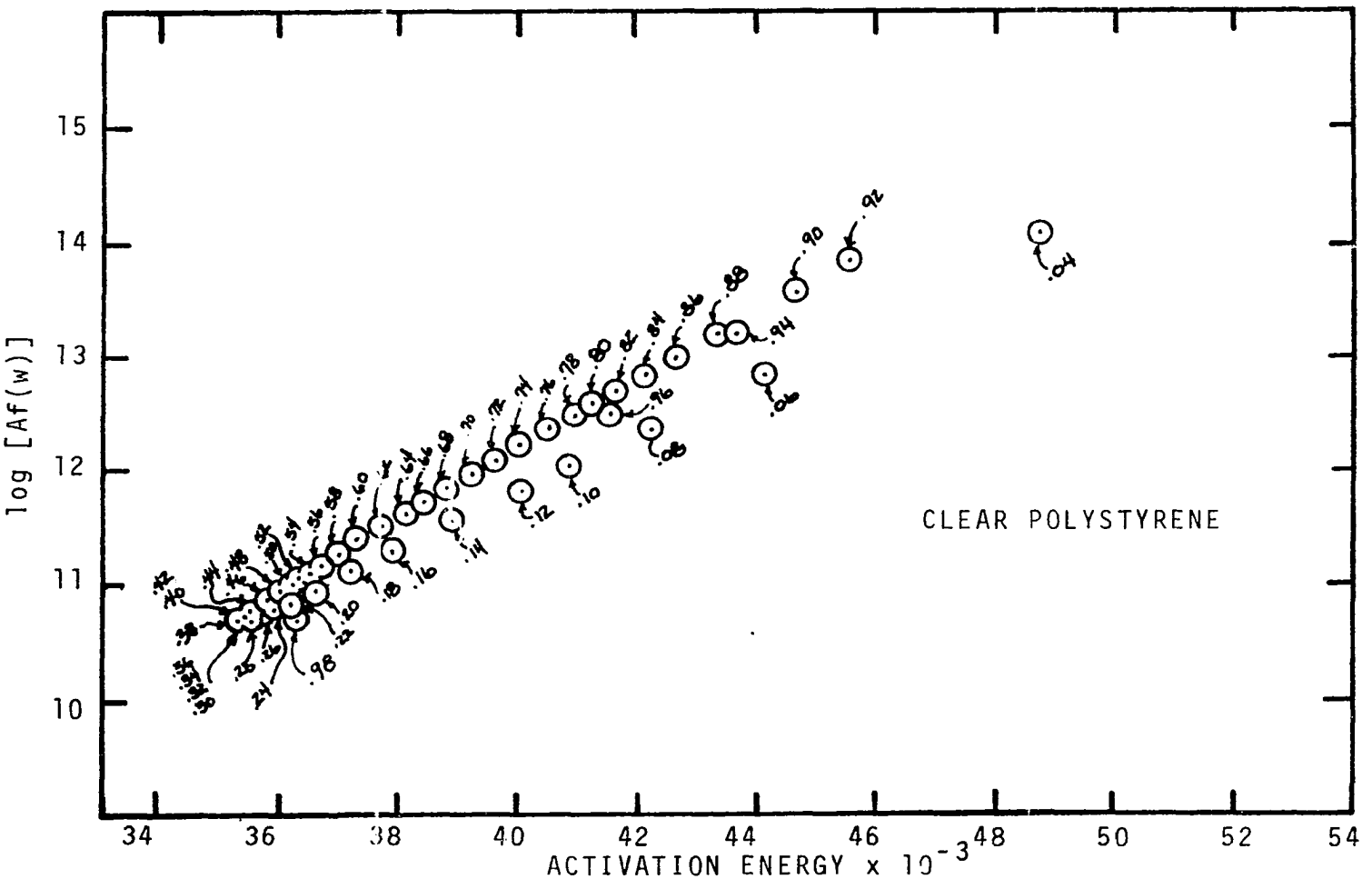

Figure IV-15. Variation in Log [Af(w)] with Activation Energy for Clear Polystyrene.

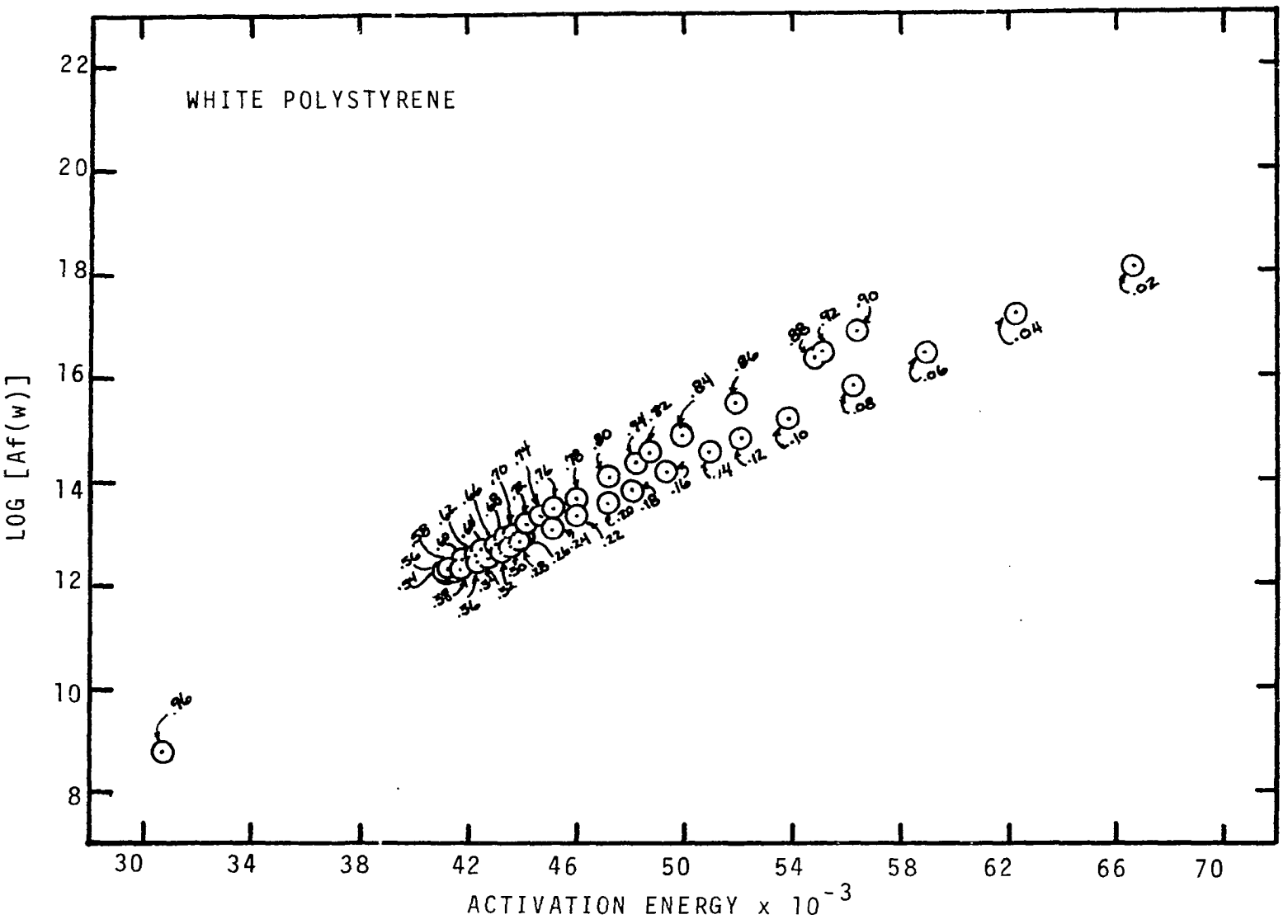

Figure IV-16. Variation in Log [Af(w)] with Activation Energy for White Polystyrene.

samples. Both of these curves show the same characteristics. As the curve is examined, going from low conversion to high conversion, three straight line portions are indicated with two inflection points. On each of these curves the points may be collapsed to essentially a single straight line in a very interesting manner. Recall that in modeling the clear polystyrene reaction with a single set of parameters, an order of 0.5 was obtained. If the f(W) in Figure IV-15 is taken to be of the form $f(W) = (W)^n$, and using $n = 0.5$, log A may be calculated as

$$\log (A) = \log [Af(W)] - n \log W \qquad \text{(IV-11)}$$

Calculating values for log A in this manner and plotting log A versus E, a single straight line is obtained. The slope of the straight line is 0.311×10^{-3} and the intercept is -0.22. This same procedure is carried out for the white polystyrene, this time using an order of 0.9. Again a straight line is obtained with a slope of 0.302×10^{-3} and an intercept of -0.96. These two lines are very nearly the same and in fact are almost exactly the same as the lines obtained in Figures IV-3 and IV-4 by the first method of analysis.

Polymethylmethacrylate Weight Loss Kinetics

In examining the rate of weight loss curves in Figures III-17 through III-21 at least two and possibly three separate weight loss steps are evident. The first of these is

obvious especially at the lower heating rates. This first step, however, only accounts for approximately 10 percent of the total weight loss. Irregularities are seen in the rising portion of the major peak, while the portion from just before the peak to completion is smooth, which indicates the possibility of at least two other weight loss steps in this portion of the degradation. Regardless of these facts, it was decided, due to the relatively smooth shape of the weight loss curve, to try to model the weight loss kinetics with a single term expression. The method used was identical to the one used with polystyrene. Table IV-3 presents the results of fitting each heating rate with its own set of kinetic parameters. A comparison of the experimental and calculated weight loss curves is given in Figure IV-17.

TABLE IV-3

INDIVIDUAL KINETIC PARAMETERS USED TO MODEL PMMA WEIGHT LOSS KINETICS

Heating Rate (°C/min)	log A	E (cal/mole)	n
10	3.84	13,386.	0.465
20	5.00	16,181.	0.424
40	5.38	16,906.	0.292
80	5.86	18,162.	0.243
160	6.55	19,708.	0.236

Figure IV-18 is a plot of log A versus E using the values presented in Table IV-3. It was attempted, using the

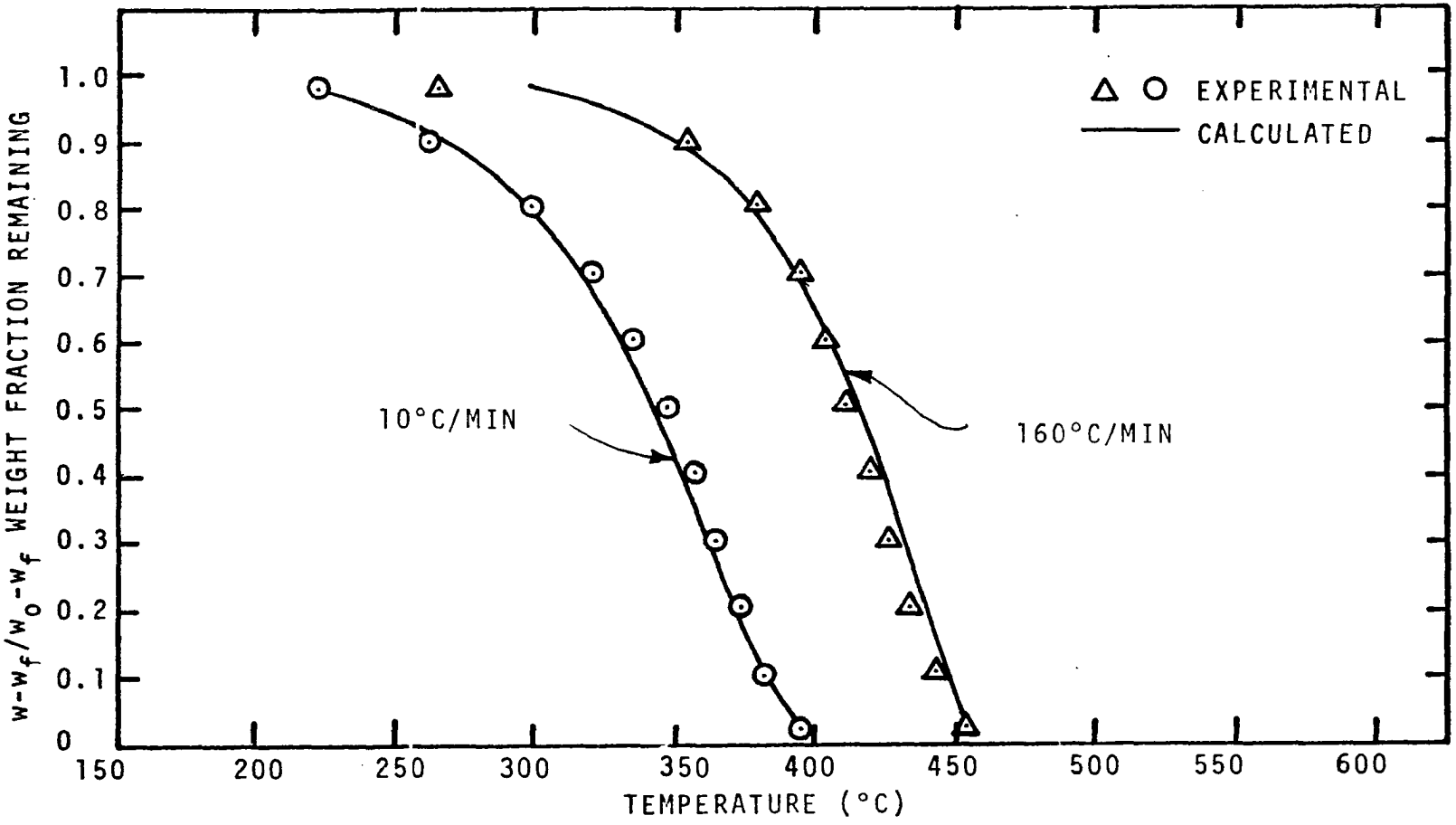

Figure IV-17. Comparison of Experimental and Calculated PMMA Weight Loss Using "Best" Kinetic Parameters.

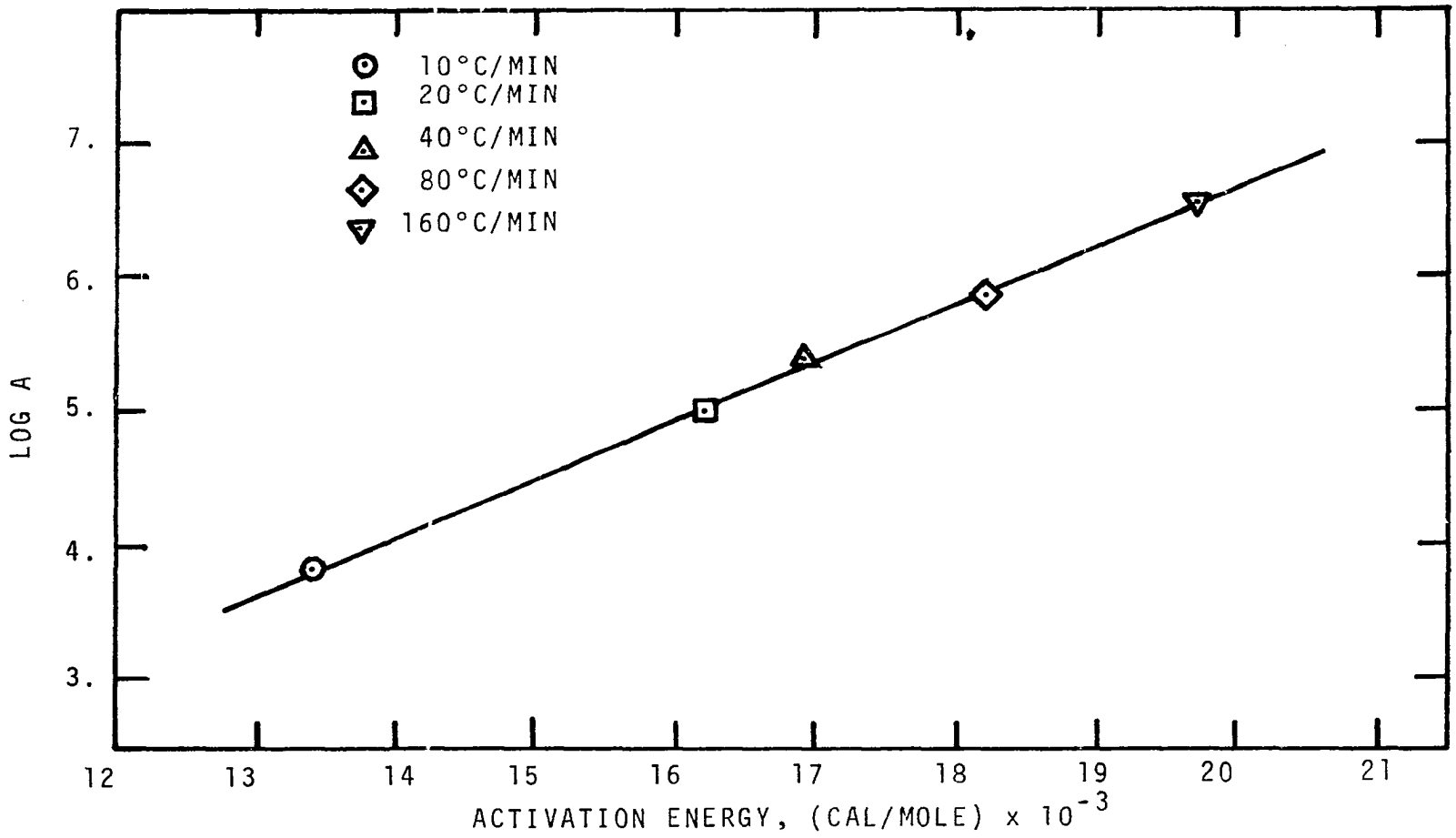

Figure IV-18. Relationship Between E and Log A for Polymethylmethacrylate.

same technique described for polystyrene, to obtain a single set of kinetic parameters that would model the PMMA decomposition. The kinetic parameters obtained using this technique are shown in Table IV-4. Figure IV-19 shows the calculated and experimental weight loss curves using the parameters given in Table IV-4. As this figure shows, the attempt to model PMMA decomposition with a single set of kinetic parameters was unsatisfactory.

TABLE IV-4

SINGLE SET OF PMMA KINETIC PARAMETERS FOR ALL HEATING RATES

log A	E (cal/mole)	n
6.53	19,700.	0.90

The kinetic parameters obtained by fitting each heating rate individually showed a fairly consistant variation with heating rate. Log A, E, and n are plotted against ln β in Figures IV-20 through IV-22. Kinetic parameters were obtained as a function of heating rate as indicated by the straight lines in these figures. These parameters are given in Table IV-5, and a comparison of calculated weight loss curves, using these parameters, with experimental data is given in Figure IV-23. As this figure indicates, this technique is much more successful in modeling the weight loss kinetics of polymethylmethacrylate decomposition.

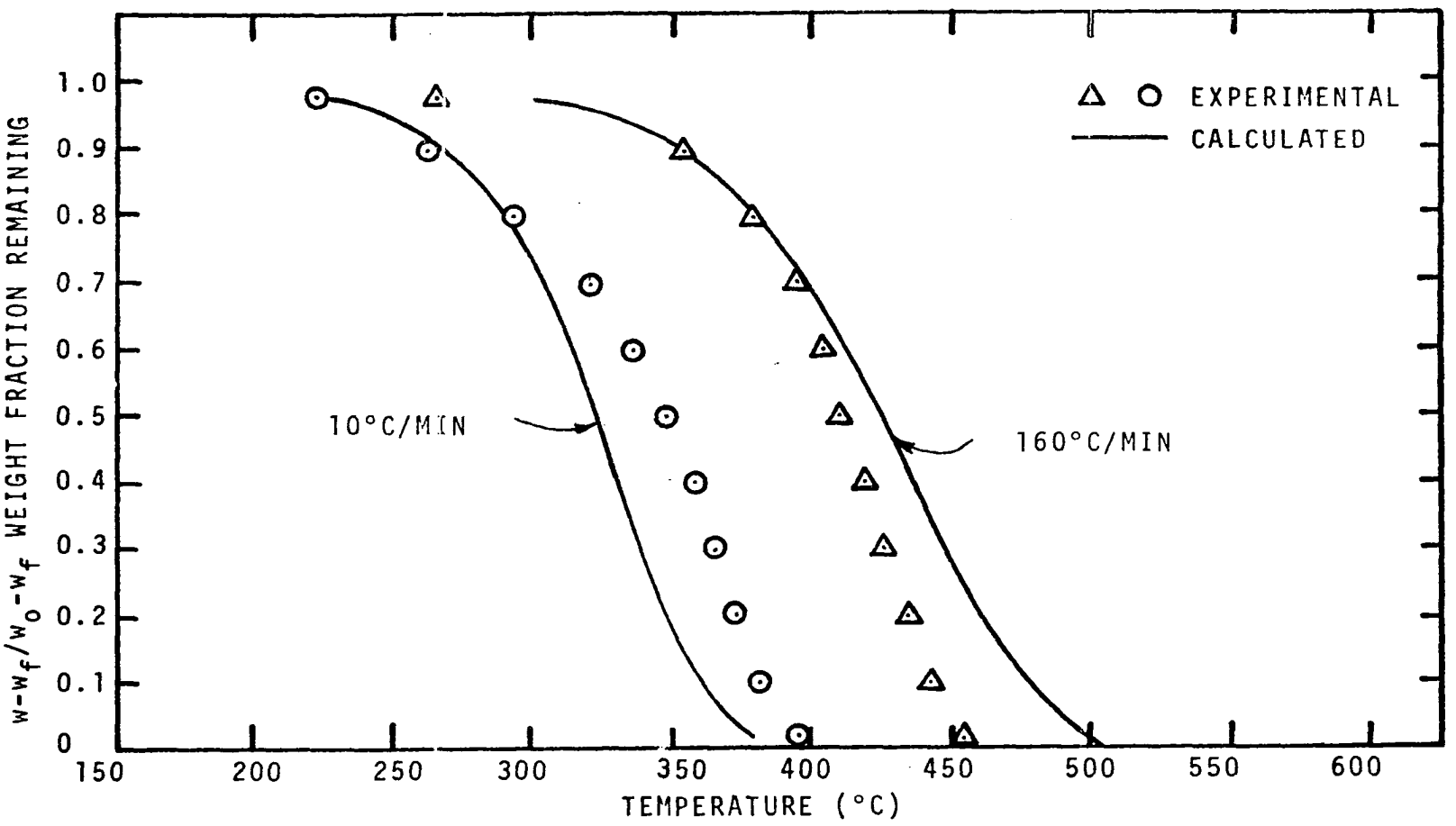

Figure IV-19. Comparison of Polymethylmethacrylate Experimental and Calculated Weight Loss Curves Using a Single Set of Kinetic Parameters.

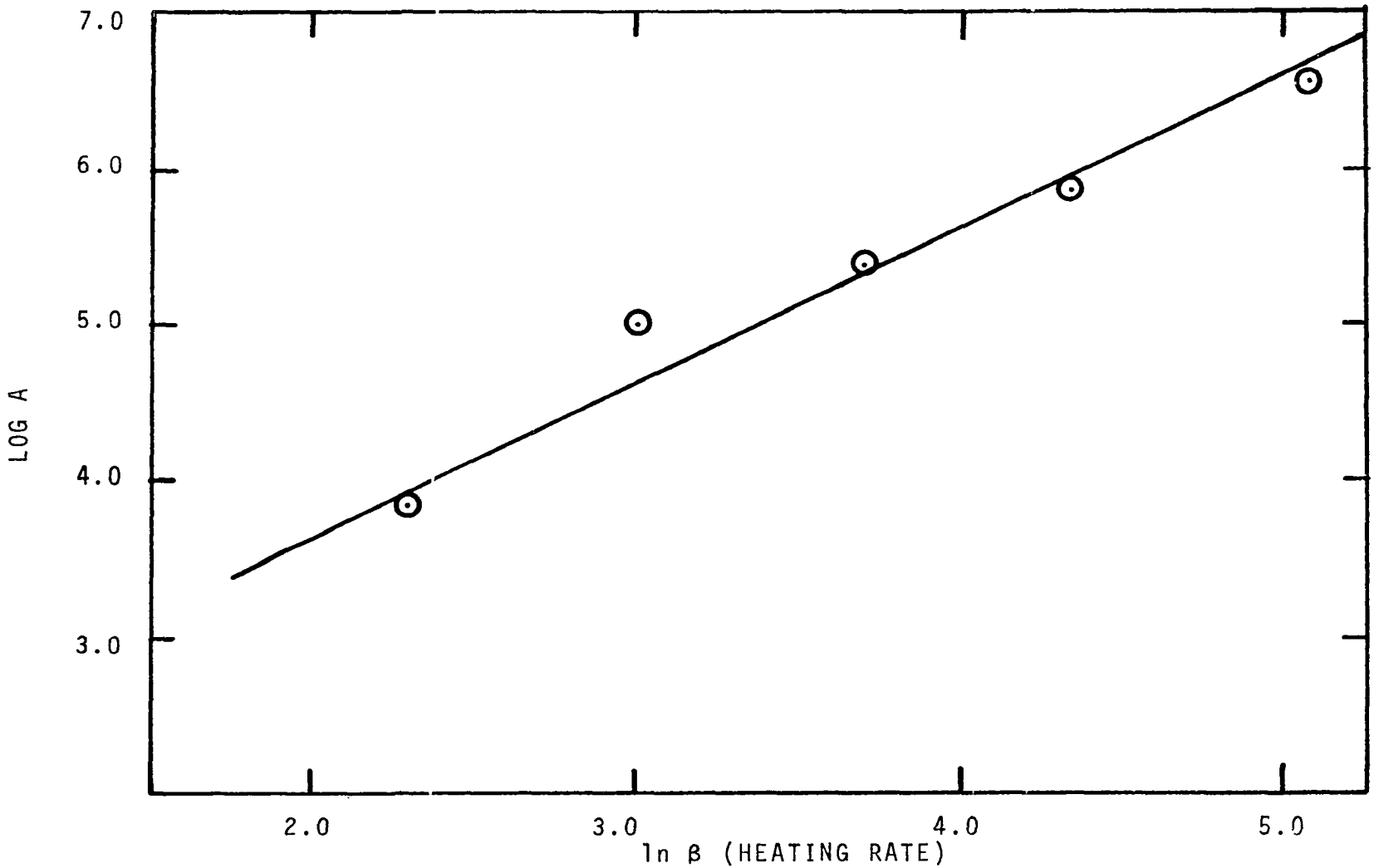

Figure IV-20. Variation of Log A with Heating Rate for Polymethylmethacrylate.

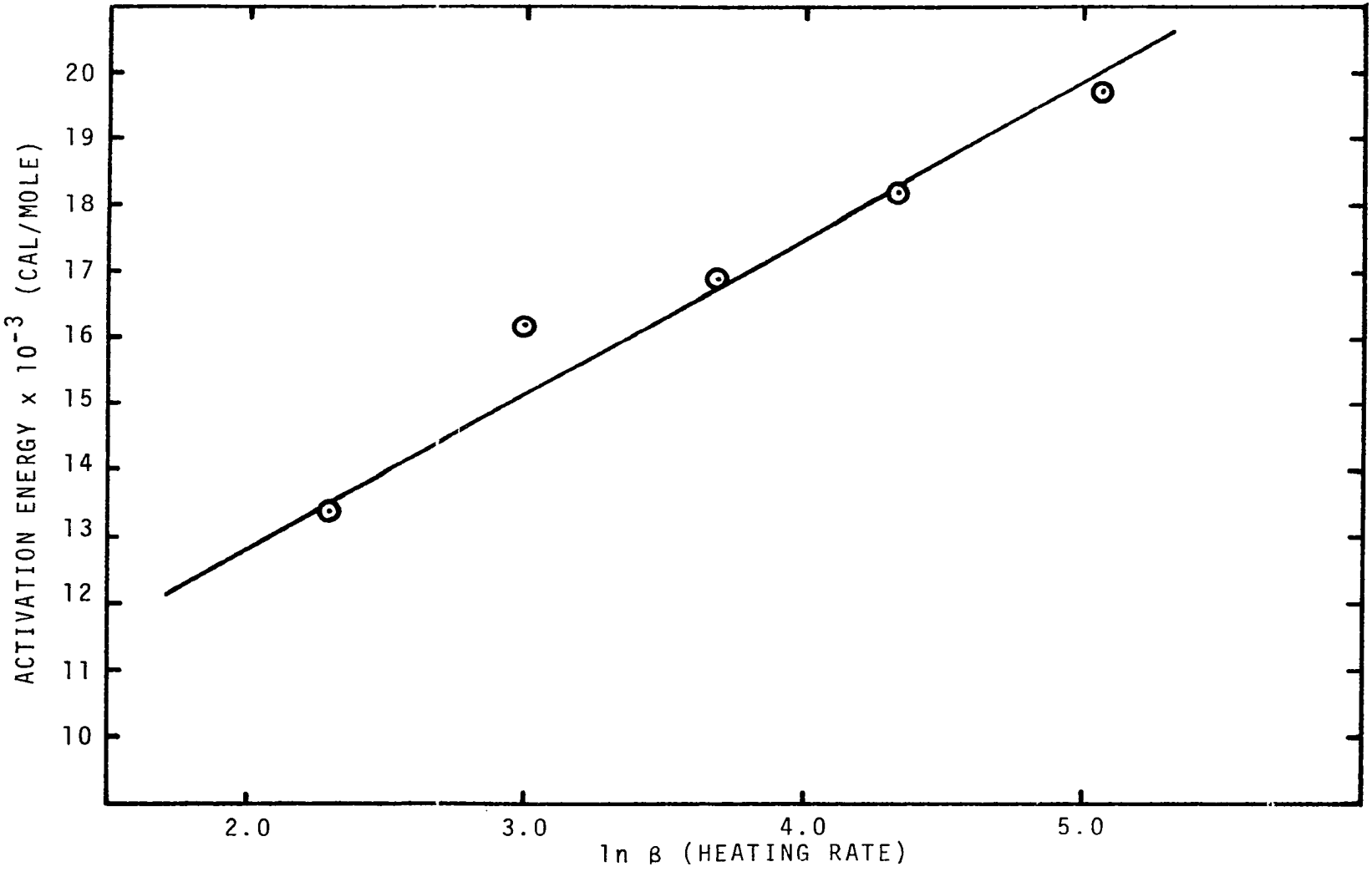

Figure IV-21. Relationship Between Activation Energy and Heating Rate for Polymethylmethacrylate.

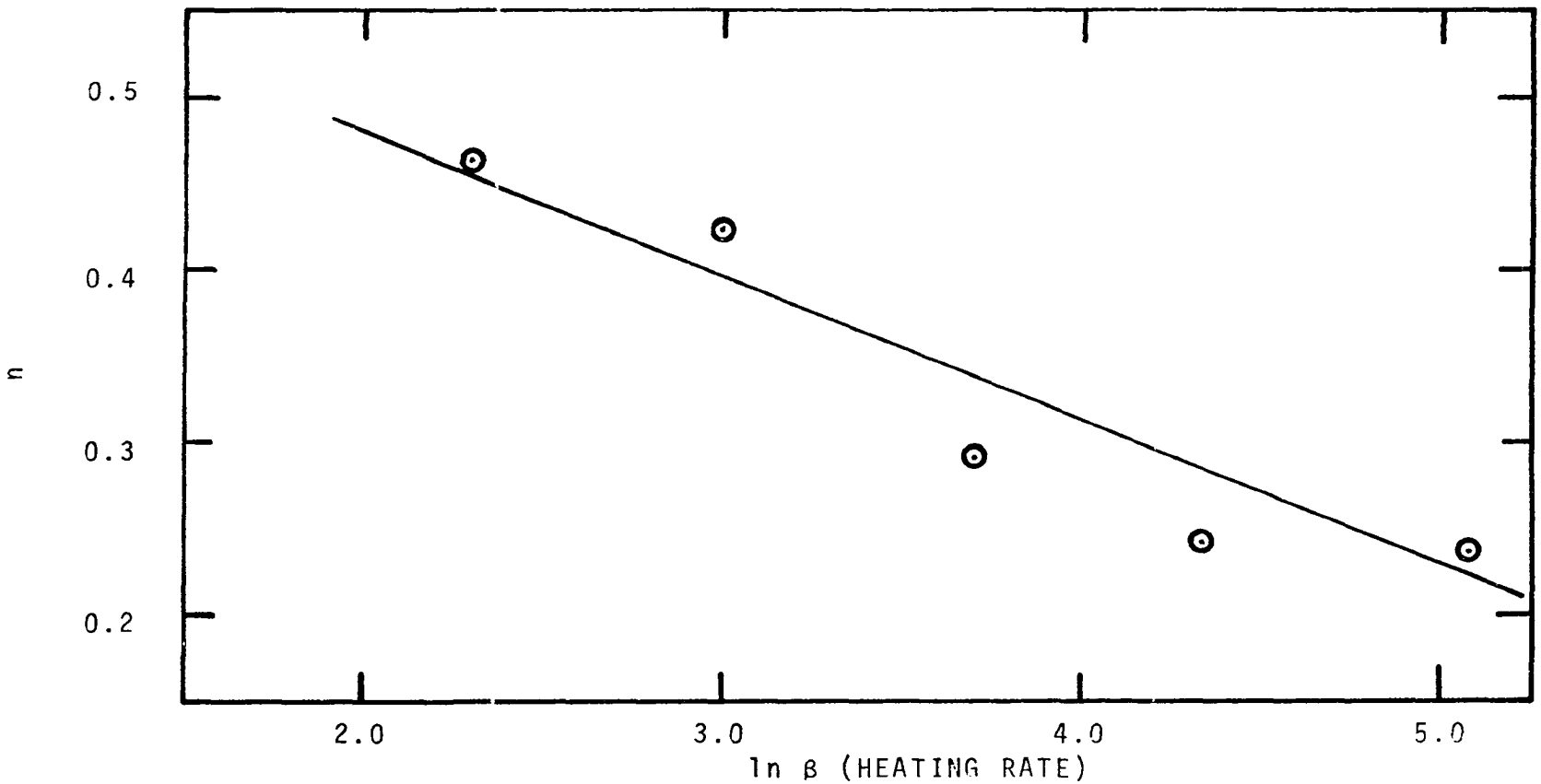

Figure IV-22. Relationship Between Reaction Order and Heating Rate for Polymethylmethacrylate.

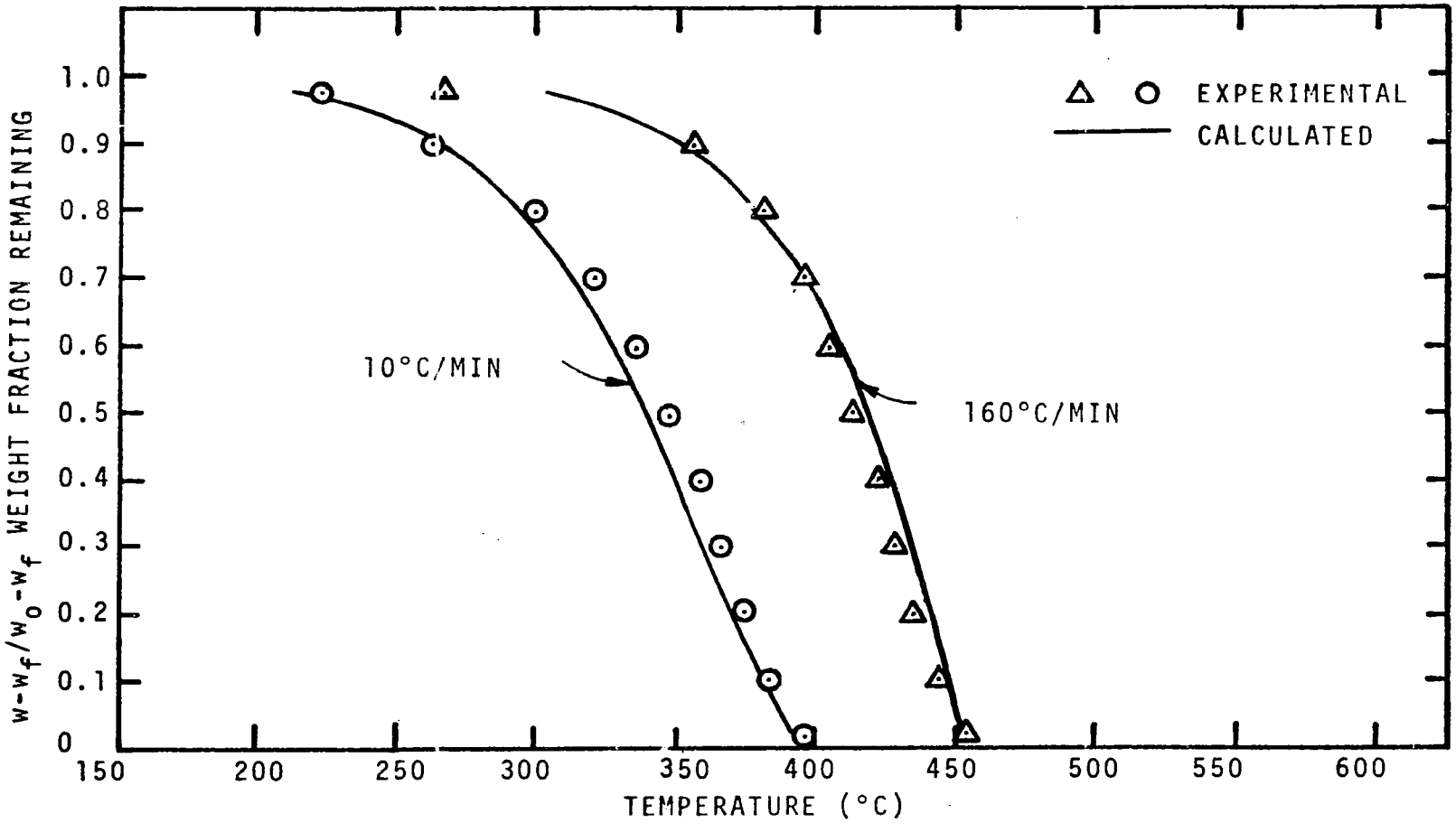

Figure IV-23. Comparison of Experimental and Calculated Weight Loss Curves for Polymethyl Methacrylate. Kinetic Parameters a Function of Heating Rate.

TABLE IV-5

KINETIC PARAMETERS OBTAINED AS A FUNCTION OF HEATING RATE FOR POLYMETHYLMETHACRYLATE

Heating Rate (°C/min)	log A	E (cal/mole)	n
10	3.92	13,500.	0.45
20	4.58	15,100.	0.40
40	5.36	16,900.	0.34
80	5.96	18,300.	0.28
160	6.67	20,100.	0.22

Friedman's method of analysis was also applied to PMMA degradation data. The results of the application of this technique are presented graphically in Figures IV-24 and IV-25. The early peak observed in the rate of weight loss curve for PMMA (this peak is most evident in the 10°C/min curve) is characterized by the low activation energies shown in Figure IV-24 during the initial weight loss period. The second peak in the PMMA dW/dt curves is characterized by much higher activation energies. As in the case of polystyrene, we have no definite evidence as to whether this second peak is a single activation energy process or whether the activation energy is actually changing with conversion. Using an average activation energy of 34,700. cal/mole, Figure IV-25 indicates the last 80 percent of this decomposition to be nearly a first order process.

One of the striking features of the results of these two methods of kinetic analysis is the large difference in

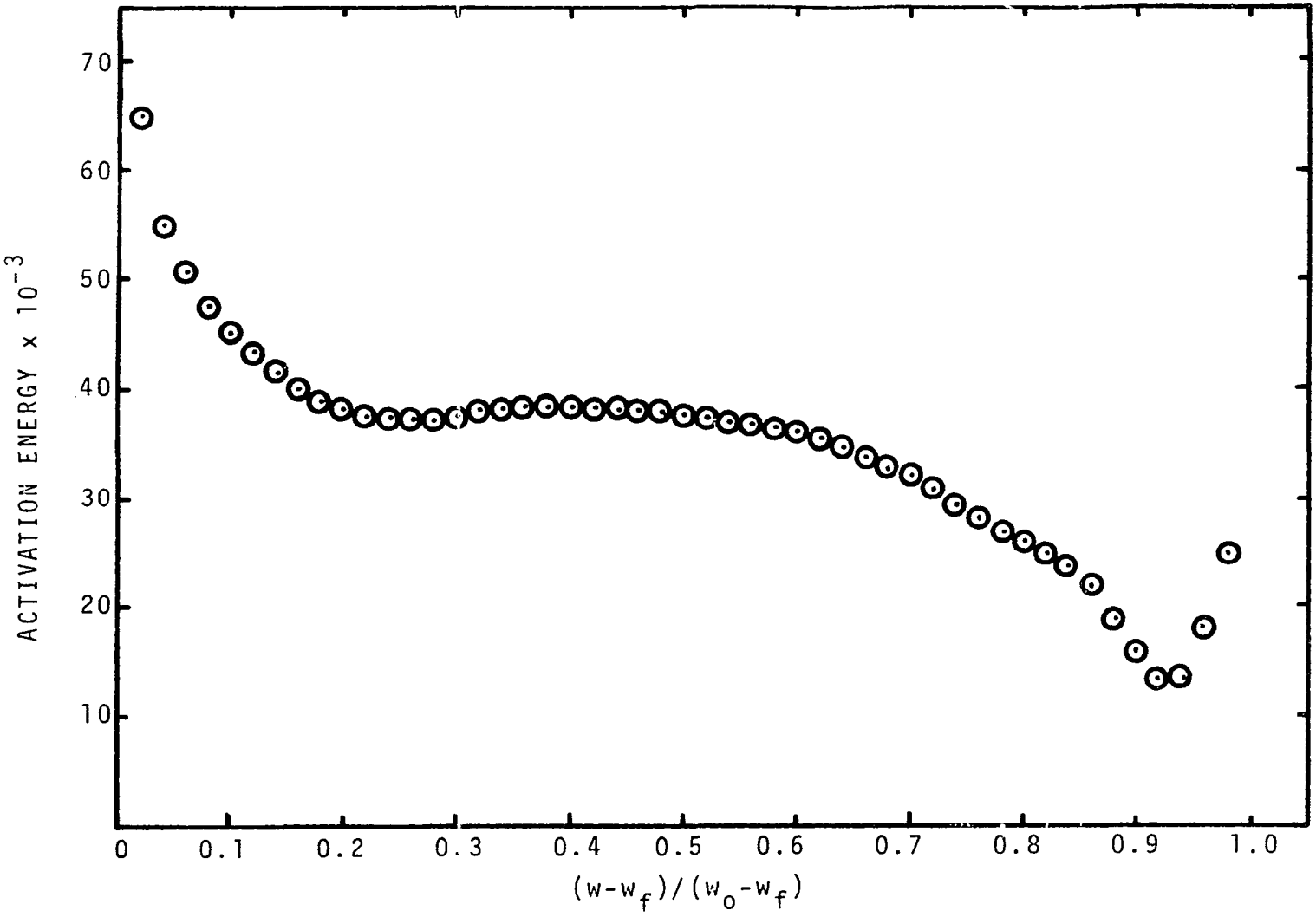

Figure IV-24. Variation of Activation Energy with Conversion for Polymethylmethacrylate. Method of Friedman.

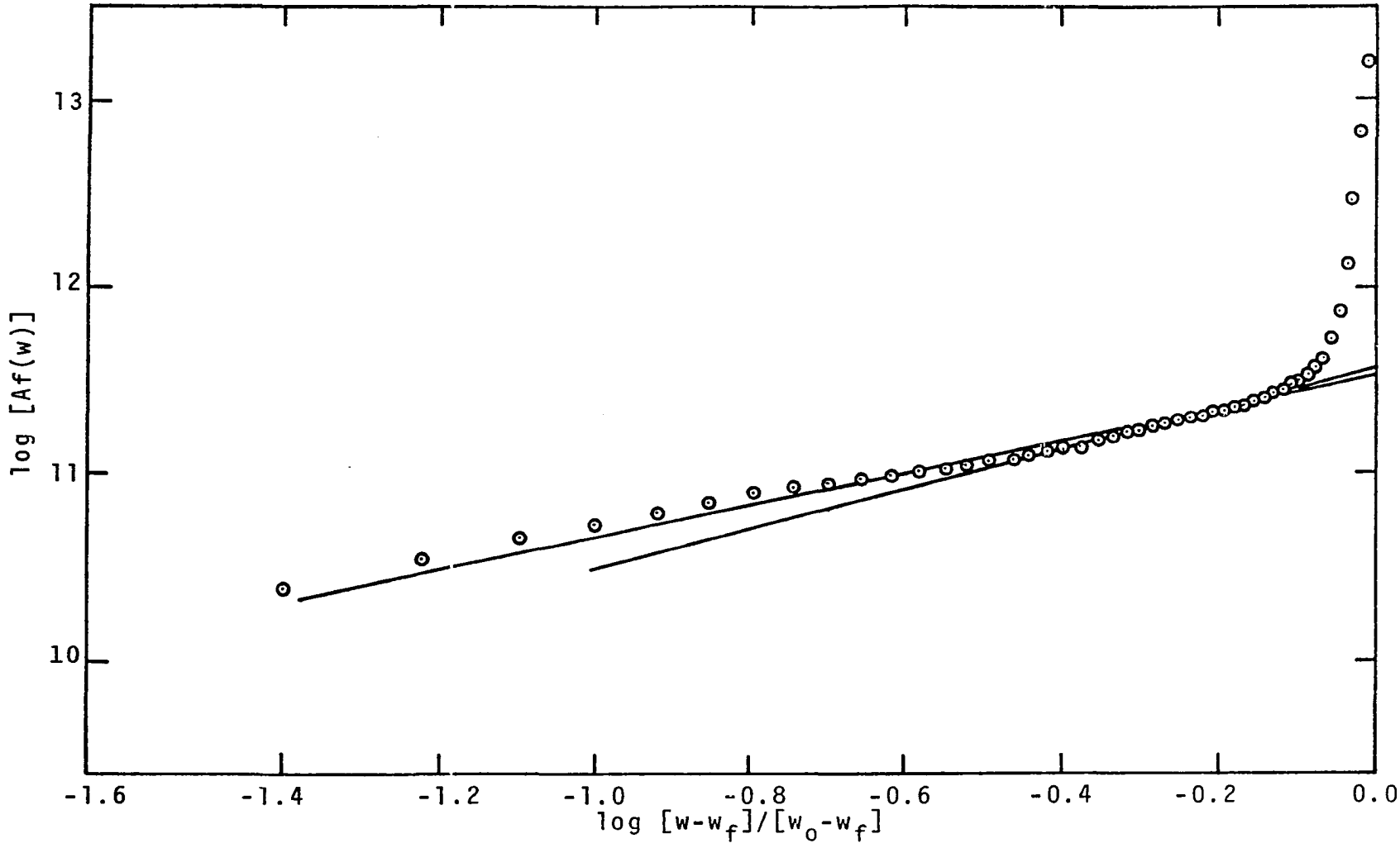

Figure IV-25. Plot of Log [Af(w)] Against Log W for Polymethylmethacrylate. Method of Friedman.

kinetic parameters indicated. The early weight loss step in the PMMA degradation seems to completely dominate the selection of kinetic parameters by the first technique. Although these parameters allow the weight loss kinetics to be modeled quite adequately, it is felt that the parameters indicated by the Friedman method of analysis are probably more indicative of the actual kinetics of the major portion of the weight loss process.

Polyvinyl Chloride Weight Loss Kinetics

Due to the complex nature of the PVC degradation curves, no attempt was made to model this decomposition with a single term kinetic expression. The method of Friedman was applied to the data of the two PVC samples. The results of the application of this technique are shown in Figure IV-26 through IV-29. While the curves shown in these figures for the two PVC samples are similar in nature, Figures IV-28 and IV-29 seem to give the more distinctive description of the degradation process.

In the rate of weight loss curves shown in Figures III-22 and III-23 three distinct weight loss steps may be observed. The initial large peak is the first step. On the downslope of this large peak, beginning at approximately 35 percent weight loss, the second step becomes recognizable. After the reaction has slowed to almost a complete halt, the third step is seen to begin and is characterized by the final

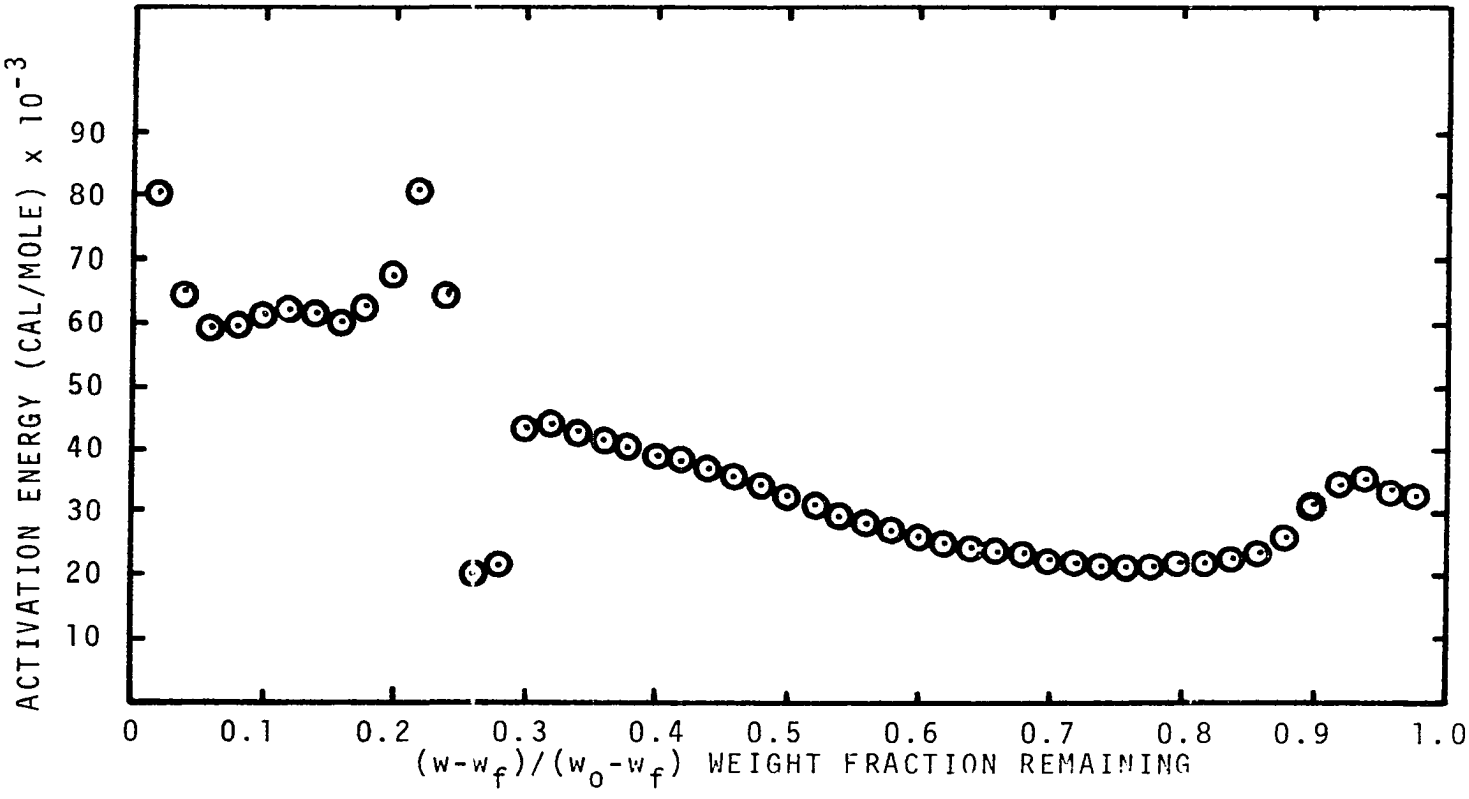

Figure IV-26. Variation in Activation Energy with Conversion for Clear Polyvinylchloride. Method of Friedman.

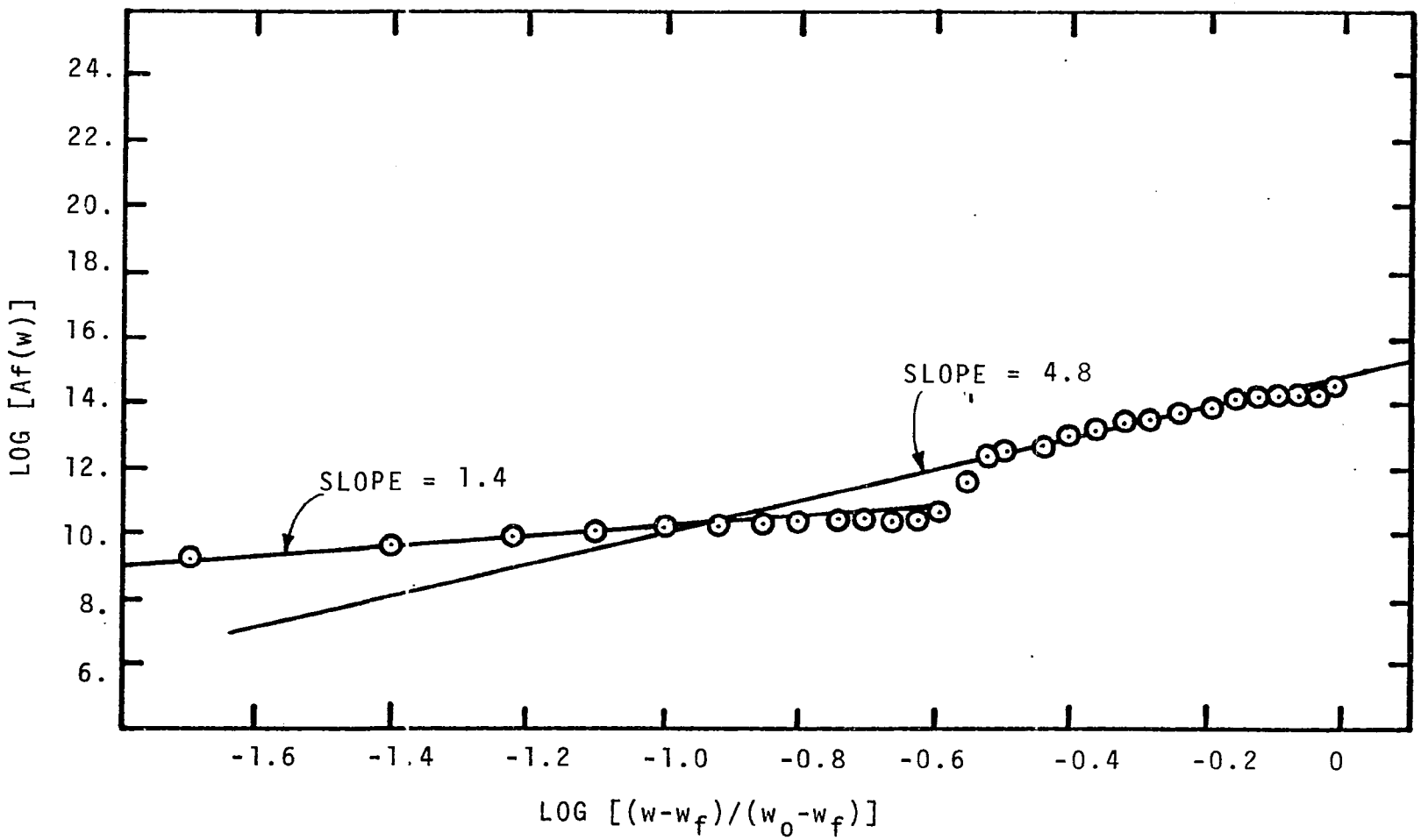

Figure IV-27. Variation in Log [Af(w)] with Log $[(w-w_f)/(w_o-w_f)]$ for Clear Polyvinyl Chloride. Method of Friedman.

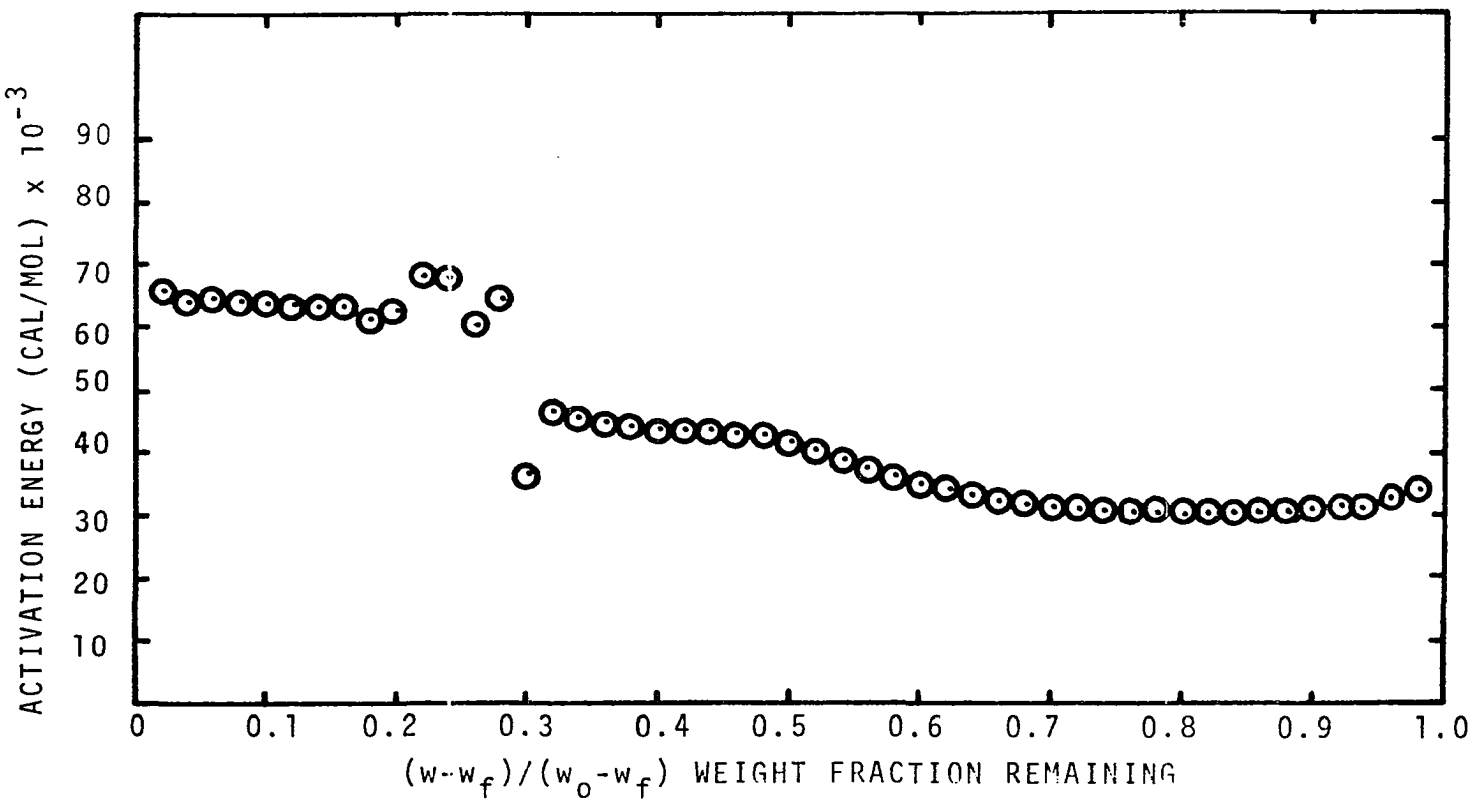

Figure IV-28. Variation in Activation Energy with Conversion for Unstabilized Polyvinyl Chloride. Method of Friedman.

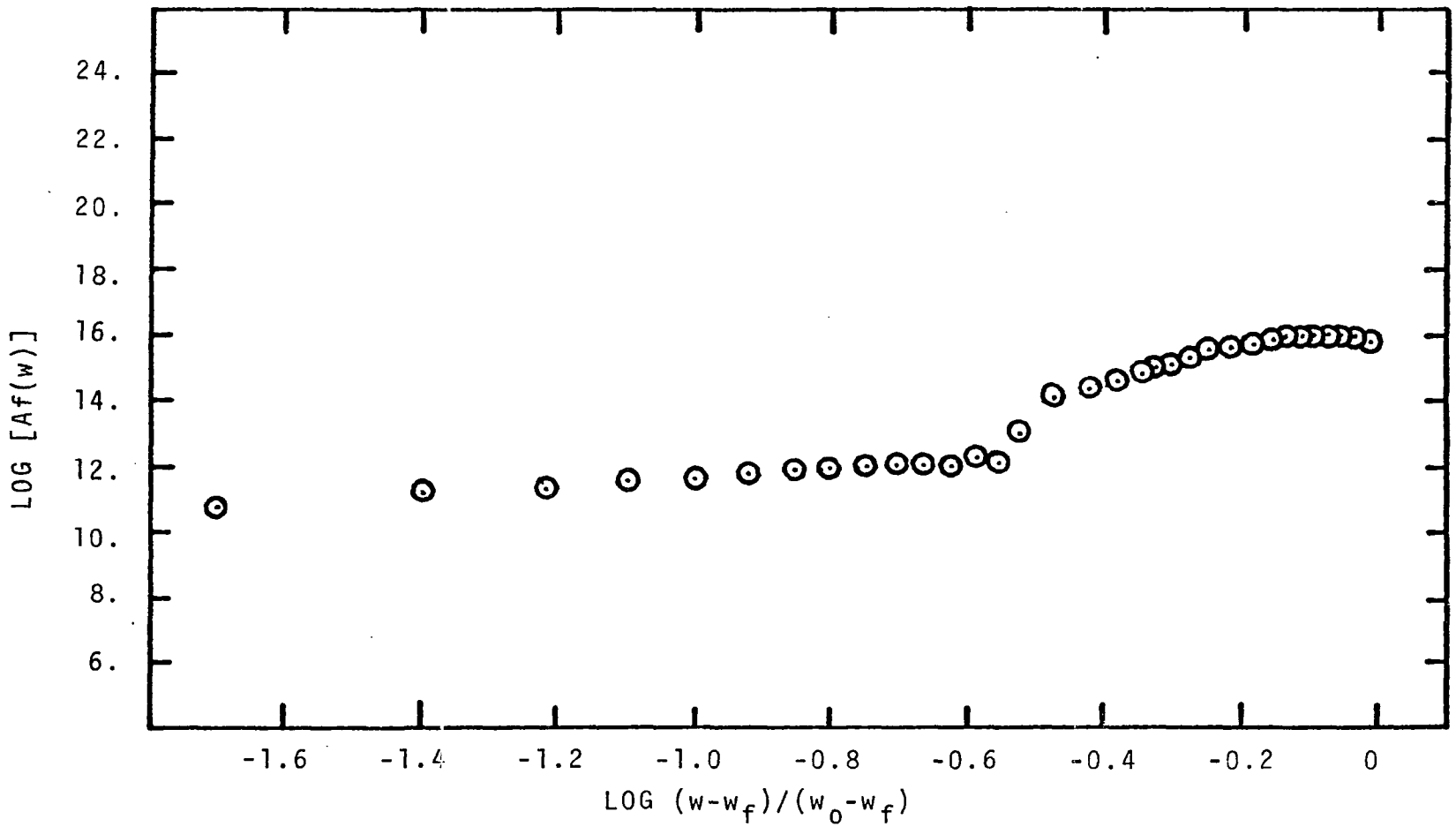

Figure IV-29. Variation in Log [Af(w)] with Log $(w-w_f)/(w_o-w_f)$ for Unstabilized Polyvinyl Chloride. Method of Friedman.

single peak. These three steps may be seen clearly in Figure IV-28. From the onset of degradation to 30 percent total weight loss, the activation energy is shown to be very nearly constant at 30,000 cal/mole. The activation energy then begins to change, indicating where the first and second weight loss steps overlap, but again becomes nearly constant from 50 percent to 78 percent total weight loss. The activation energy for this second step is about 43,000 cal/mole for the unstabilized PVC. The last step, from 82 percent to 100 percent weight loss, is characterized by an activation energy of 64,000 cal/mole. Figures IV-27 and IV-29 are not applicable in determining a reaction order for an individual reaction step in PVC degradation. In calculating the log [Af(W)] values, the rate of weight loss must be based only on the weight lost in the individual step under consideration. The one exception is a zero order reaction. A zero order reaction will be accurately indicated even though the log [Af(W)] values are based on the total weight lost in the reaction. Therefore, the only reaction step for which an order may be obtained from Figures IV-27 and IV-29 is the first one, which is clearly indicated to be of zero order.

Decomposition Energies of Polystyrene and Polymethylmethacrylate

The decomposition energies of two polystyrene samples and the PMMA sample may be obtained directly from Figures

III-34 through III-45 by integration of the dE/dt curves. The results of this integration are presented in Table IV-6. The output signal from the DSC-1b is a measure of the total energy change occurring in the sample at any particular instant. It is assumed here that the total energy change occurring in these samples is due only to heat capacity effects and decomposition energy effects. Before the dE_d/dt curves shown in Figure III-34 through III-45 are obtained the heat capacity effects must be removed from the output curves obtained from the DSC-1b. The onset of decomposition as indicated by the TGA data is used to define the onset of decomposition on the dE_d/dt durves. From this point the energy required by the sample due to the sample heat capacity is assumed to decrease in direct proportion to the decrease in sample weight. These two assumptions allow the energy of decomposition to be obtained from the total "energy capacity" curves given by the DSC-1b. An example of the application of this procedure is shown in Figure IV-30. The total energy curve is as taken directly from the DSC-1b. The area under this curve attributed to decomposition is indicated separately from the energy due to heat capacity effects.

In comparing the dE_d/dt curves with the dW/dt durves, shown in Figures III-34 through III-45, it may be observed that in all cases the two curves are very similar in appearance. This indicates, from a qualitative standpoint, that the energy curves reveal no degradation mechanisms not observable in the

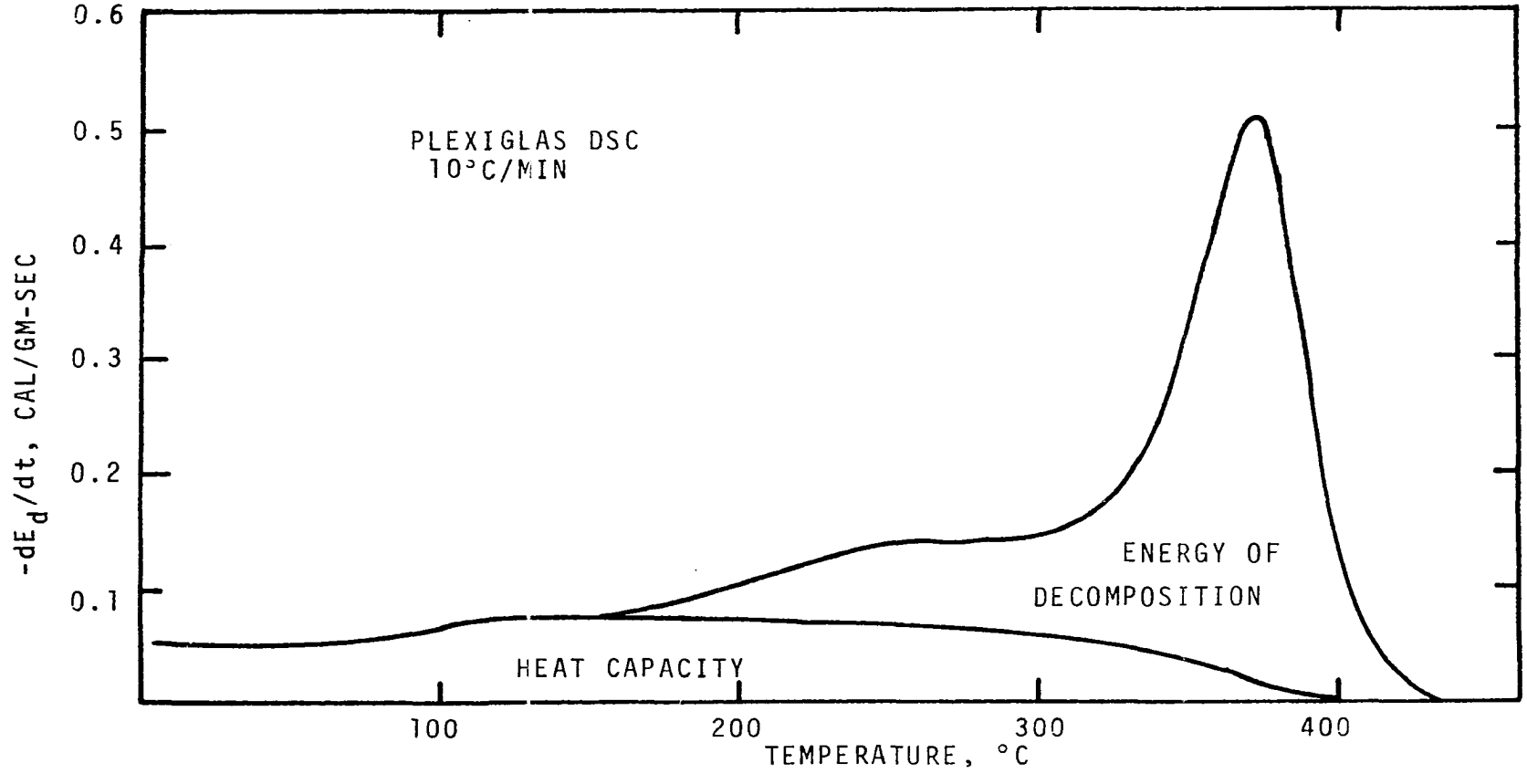

Figure IV-30. Energy Changes Occurring During the Decomposition of Polymethylmethacrylate.

TABLE IV-6

DECOMPOSITION ENERGIES OF POLYSTYRENE AND POLYMETHYLMETHACRYLATE

	Heating Rate (°C/min)	Endothermic Energy of Decomposition (cal/gm)
Clear Polystyrene	10	211.
	20	241.
	40	203.
	80	215.
White Polystyrene	10	196.
	20	192.
	40	188.
	80	180.
Polymethylmethacrylate	10	208.
	20	224.
	40	193.
	80	199.

weight loss data. The lack of a consistant variation in decomposition energy with heating rate is an indication that the degradation kinetics are not a function of heating rate. However, if two independent kinetic mechanisms produced nearly equal energy changes the total decomposition energy would not vary even though the degradation mechanism did change.

Degradation Dependence on Heating Rate

Before the kinetic dependence on heating rate may be discussed, it must be properly defined. If only one mechanism accounts for the polymer weight loss, the degradation will be defined as being non-heating rate dependent even though, as

was shown, the weight loss will occur at higher temperatures as the heating rate increases. If more than one mechanism accounts for the weight loss the degradation will be defined as being non-heating rate dependent if the fractional weight loss attributed to a single mechanism does not change as the heating rate is changed. Assume that a polymer degrades by two competitive weight loss mechanisms, one with an activation energy of 30,000 cal/mole and the other with an activation energy of 60,000 cal/mole. In general the step with the smaller activation energy will occur at lower temperatures than the step with the larger activation energy. At a low heating rate this polymer might degrade completely by the 30,000 cal/mole process. At higher heating rates this polymer would degrade partially by the 30,000 cal/mole process and partially by the 60,000 cal/mole process. According to the definition given here this degradation would be heating rate dependent. Consider another polymer that degrades by two independent mechanisms with these same two activation energies. At low heating rates two peaks would be observed on the dW/dt curve, one due to the 30,000 cal/mole process and one due to the 60,000 cal/mole process. As the heating rate is increased these two peaks will tend to merge until, at a high enough heating rate, only one peak would be observed. Since the shape of the dW/dt curves for this reaction are changing with heating rate it might seem that the kinetics of the degradation are dependent on heating rate. However,

since the two mechanisms of degradation are independent, according to the definition given here this reaction is non-heating rate dependent.

With this definition in mind the dependence of the polymer degradations studied here may be discussed. PMMA and PVC show no evidence of heating rate dependence. The results of the Friedman method of analysis indicate that PMMA degrades by two independent reactions and that PVC degrades by three independent mechanisms. According to the definition given here these degradations are not dependent on heating rate. The dependence of polystyrene decomposition on heating rate is much more difficult to conclude. While the PMMA and PVC dW/dt curves clearly indicate independent reactions, a distinction between one weight loss mechanism or two (or more) competitive mechanisms cannot be drawn from the polystyrene dW/dt curves. Two bits of evidence, although not conclusive, tend to indicate that the polystyrene degradation is not heating rate dependent. They are the fact that the polystyrene decomposition may be accurately modeled at all heating rates with a single set of kinetic parameters and the lack of a consistent variation in the decomposition energies.

CHAPTER V

SUMMARY AND POSSIBILITIES FOR FURTHER STUDY

The thermal degradation kinetics of polystyrene, PMMA, and PVC as revealed by weight and energy changes during pyrolysis have been studied and discussed. Kinetic parameters were obtained allowing the weight loss characteristics of the polystyrene and PMMA reactions to be accurately modeled. The total energy of decomposition was presented for polystyrene and PMMA. Individual reaction steps, as revealed by the Friedman method of data analysis, were presented for PMMA and PVC. A definition of heating rate dependence was given and the degradation of polystyrene, PMMA, and PVC discussed in the light of this definition. The kinetic parameters for the five polymer samples that are felt to be the most representative of the degradation process are summarized in Table V-1.

This study suggests several interesting areas of continued study. A method is needed for extracting kinetic parameters from the decomposition energy data. Using both the energy data and weight loss data to obtain kinetic parameters might enable a more precise definition of degradation mechanisms to be made and might also give more meaningful

TABLE V-1

SUMMARY OF KINETIC PARAMETERS

	Heating Rate (°C/min)	E (cal/mole)	log A	n
Clear Polystyrene	All	54,800.	14.1	0.50
White Polystyrene	All	42,101.	12.7	0.90
Polymethyl-methacrylate	10	13,500.	3.92	0.45
	20	15,100.	4.58	0.40
	40	16,900.	5.36	0.34
	80	18,300.	5.96	0.28
	160	20,100.	6.67	0.22
Clear Polyvinyl Chloride	All			
	(0-30% Conv.)	21,500.	--	0.
	(30-70% Conv.)	44,000.	--	--
	(70-100% Conv.)	61,000.	--	--
Unstabilized Polyvinyl Chloride	All			
	(0-30% Conv.)	30,500.	--	0.
	(30-70% Conv.)	44,000.	--	--
	(70-100% Conv.)	63,000.	--	--

kinetic parameters. A systematic method of obtaining kinetic parameters to be used in a multi-step model of complex decompositions, such as PMMA and PVC, is needed. Possibly a combination of the two methods of data analysis used in this work could be developed. The relationships between log A and E presented in this work are interesting but difficult to explain. The meaning of these relationships could be investigated. Polymers such as polystyrene, polyethylene, and polypropylene, which give smooth dW/dt curves should more readily lend themselves to this type of study.

REFERENCES CITED

1. Havens, J. A. "Thermal Decomposition of Wood." Unpublished Ph.D. dissertation. University of Oklahoma, Norman, Oklahoma, 1969.

2. Brown, L. E. "An Experimental and Analytic Study of Wood Pyrolysis." Unpublished Ph.D. dissertation. University of Oklahoma, Norman, Oklahoma, 1972.

3. Madorsky, S. L. Thermal Degradation of Organic Polymers. New York: Interscience Publishers, 1964.

4. Staudinger, H.; Brunner, M.; Frey, K.; Garbsh, P.; Singer, R.; and Wherli, A. "Highly Polymerized Compounds. XIV. Polystyrene, a Model of Rubber." Ber., 62B, 241 (1929); Ann., 468, 1 (1929).

5. Jellinek, H. H. G. "Thermal Degradation of Polystyrene. Part I." Journal of Polymer Science, III (1948), 850-865.

6. Jellinek, H. H. G. "Thermal Degradation of Polystyrene. Part II." Journal of Polymer Science, III (1949), 1-12.

7. Jellinek, H. H. G. "Thermal Degradation of Polystyrene and Polyethylene. Part III." Journal of Polymer Science, IV (1949), 13-36.

8. Madorsky, S. L. "Rates of Thermal Degradation of Polystyrene and Polyethylene in a Vacuum." Journal of Polymer Science, IX (1952), 133-156.

9. Grassie, N. "Degradation." Encyclopedia of Polymer Science and Technology, 4 (1966), 647-716.

10. Jellinek, H. H. G. "Depolymerization." Encyclopedia of Polymer Science and Technology, 4 (1966), 740-793.

11. Conley, R. T., ed. Thermal Stability of Polymers. New York: Marcel Dekker, Inc., 1970.

12. Anderson, D. A., and Freeman, E. S. "The Kinetics of the Thermal Degradation of Polystyrene and Polyethylene." Journal of Polymer Science, 54 (1961), 253-260.

13. Freeman, E. S., and Carroll, B. "The Application of Thermoanalytical Techniques to Reaction Kinetics." Journal of Physical Chemistry, 62 (1958), 394.

14. Wall, L. A.; Straus, S.; Flynn, J. H.; and McIntire, D. "The Thermal Degradation Mechanism of Polystyrene." Journal of Physical Chemistry, 70, 1 (1966), 53-62.

15. Wegner, J., and Patat, F. "Thermal Degradation of Polystyrene." Journal of Polymer Science: Part C, 31 (1970), 121-135.

16. Wall, L. A., and Flynn, J. H. "Degradation of Polymers." Rubber and Chemistry Technology, 35 (1962), 1157-1221.

17. Madorsky, S. L. Thermal Degradation of Organic Polymers. New York: Interscience Publishers, 1964, 26-89.

18. Levi, D. W. "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers." Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, New Jersey. Note 7 (1963).

19. Teetsel, D. A., and Levi, D. W. "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers II." Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, New Jersey. Note 10 (1966).

20. Teetsel, D. A., and Levi, D. W. "Literature Survey on Thermal Degradation, Thermal Oxidation, and Thermal Analysis of High Polymers III." Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, New Jersey. Note 20 (1969).

21. Wall, L. A. "Pyrolysis of Polymers." Paper presented at the Fourth Materials Research Symposium of the National Bureau of Standards, 1970.

22. Burningham, N. W. "Thermal Decomposition of Polymers." Unpublished Ph.D. dissertation. University of Utah, 1970.

23. Reich, L. "Application of DTA Traces to Polymer Pyrolysis." Journal of Applied Sciences, 10 (1966), 813-823.

24. Madorsky, S. L. "Rates and Activation Energies of Thermal Degradation of Styrene and Acrylate Polymers in a Vacuum." Journal of Polymer Science, 11, 5 (1953), 491-506.

25. Jellinek, H. H. G., and Clark, J. E. "A New Technique for the Study of High-Polymer Degradation Reactions." Canadian Journal of Chemistry, 41 (1963), 355-362.

26. Jellinek, H. H. G., and Clark, J. E. "Thermal Degradation of Polymethylmethacrylate in a Closed System." Journal of Polymer Science, Part A, III (1965), 1171-1184.

27. Schwenker, R. F., and Garn, P. D., eds. Thermal Analysis, Vol. I. New York: Academic Press, 1969.

28. Flynn, J. H., and Wall, L. A. "General Treatment of the Thermogravimetry of Polymers." Journal of Research, NBS70A, 6 (1966), 487-523.

29. Friedman, H. L. "Kinetics of Thermal Degradation of Char Forming Plastics from Thermogravimetry--Application to a Phenolic Resin." Journal of Polymer Science, 6C (1963), 183.

30. Goldfarb, I. J.; McGuchan, R.; and Meeks, A. C. "Kinetic Analysis of Thermogravimetry. Part II. Programmed Temperature." Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. AFML-TR-68-181, Part #2 (1968).

31. Reich, L., and Stivala, S. S. Elements of Polymer Degradation. New York: McGraw-Hill Book Company, Inc., 1971.

32. Hallman, J. R. "Ignition Characteristics of Plastics and Rubber." Unpublished Ph.D. dissertation. University of Oklahoma, Norman, Oklahoma, 1971.

33. Flynn, J. H. "An Analytical Evaluation of Differential Scanning Calorimetry," Status of Thermal Analysis, National Bureau of Standards Special Publication 338, October 1970, 119.

APPENDIX

DATA FROM POLYMER TGA STUDIES

Run No.	Heating Rate (°C/min)	Initial Weight (mg)	Final Weight (mg)	Max. Rate of Wt. Loss **	Temp. at Max. Rate of Wt. Loss °C
White Polystyrene					
PS- 1-TGS	10	2.96	0.04	0.245	427.
PS- 2-TGS	10	3.74	0.02	0.237	432.
PS- 3-TGS	10	3.62	0.03	0.244	428.
PS- 4-TGS	20	3.78	0.02	0.443	445.
PS- 5-TGS	20	3.84	0.06	0.450	446.
PS- 6-TGS	20	4.30	0.03	0.471	445.
PS- 7-TGS	40	3.36	0.04	0.826	465.
PS- 8-TGS	40	2.24	0.01	0.861	462.
PS- 9-TGS	40	2.36	0.04	0.856	463.
PS-11-TGS	80	2.78	0.03	1.44	476.
PS-12-TGS	80	3.24	0.01	1.42	479.
PS-13-TGS	80	3.20	0.00	1.41	472.
PS-14-TGS	160	3.10	0.03	2.41	499.
PS-15-TGS	160	3.70	0.03	2.30	496.
PS-16-TGS	160	3.82	0.02	2.28	498.
Clear Polystyrene					
CPS- 1-TGS	10	3.78	0.00	0.287	416.
CPS- 2-TGS	10	3.68.	0.00	0.284	420.
CPS- 3-TGS	10	3.88	0.00	0.290	421.
CPS- 4-TGS	20	4.56	0.00	0.561	432.
CPS- 5-TGS	20	3.76	0.00	0.554	437.
CPS- 6-TGS	20	3.06	0.02	0.562	434.
CPS- 7-TGS	40	6.24	0.00	0.879	464.
CPS- 8-TGS	40	3.62	0.00	0.956	455.
CPS- 9-TGS	40	1.58	0.00	1.030	449.

**Units: mg/sec-mg total wt. loss.

Run No.	Heating Rate (°C/min)	Initial Weight (mg)	Final Weight (mg)	Max. Rate of Wt. Loss **	Temp. of Max. Rate of Wt. Loss °C
Clear Polystyrene, continued					
CPS-10-TGS	80	3.20	0.00	1.652	467.
CPS-12-TGS	80	3.24	0.00	1.648	468.
CPS-13-TGS	80	3.16	0.00	1.642	466.
CPS-14-TGS	160	3.26	0.00	2.678	485.
CPS-15-TGS	160	3.62	0.00	2.606	488.
CPS-16-TGS	160	3.98	0.00	2.484	491.
Polymethylmethacrylate					
PG- 1-TGS	10	3.74	0.00	0.140	372.
PG- 2-TGS	10	7.36	0.00	0.149	375.
PG- 3-TGS	10	6.74	0.00	0.141	376.
PG- 4-TGS	20	3.66	0.00	0.325	387.
PG- 5-TGS	20	2.84	0.00	0.342	390.
PG- 6-TGS	20	4.72	0.03	0.340	393.
PG- 8-TGS	40	4.76	0.00	0.621	411.
PG-10-TGS	40	2.94	0.00	0.658	402.
PG-11-TGS	40	6.84	0.02	0.630	414.
PG-12-TGS	80	3.84	0.00	1.190	427.
PG-13-TGS	80	4.18	0.00	1.176	432.
PG-14-TGS	80	4.14	0.07	1.175	436.
PG-15-TGS	160	2.58	0.02	2.013	437.
PG-16-TGS	160	2.30	0.00	1.984	437.
PG-17-TGS	160	2.38	0.00	2.029	432.
Unstabilized Polyvinyl Chloride					
EBPUC-1-TGS	10	4.56	0.54	0.152	300.
EBPUC-2-TGS	10	4.10	0.42	0.174	292.
EBPUC-3-TGS	10	6.48	0.71	0.189	296.
EBPUC-6-TGS	20	3.40	0.29	0.354	305.
EBPUC-7-TGS	20	3.63	0.25	0.346	308.
EBPUC-8-TGS	20	6.42	0.52	0.351	305.
EBPUC-9-TGS	40	3.26	0.24	0.636	322.
EBPUC-10-TGS	40	3.34	0.25	0.600	325.
EBPUC-11-TGS	40	3.48	0.26	0.690	318.
EBPUC-12-TGS	80	3.98	0.27	0.828	336.
EBPUC-13-TGS	80	5.58	0.38	0.931	341.
EBPUC-14-TGS	80	4.78	0.35	0.992	337.
EBPUC-15-TGS	160	3.24	0.18	1.692	349.
EBPUC-16-TGS	160	3.36	0.21	1.738	347.
EBPUC-17-TGS	160	3.28	0.21	1.765	347.

**Units: mg/sec-mg total wt. loss.

Run No.	Heating Rate (°C/min)	Initial Weight (mg)	Final Weight (mg)	Max. Rate of Wt. Loss **	Temp. at Max. Rate of Wt. Loss °C
Clear Polyvinyl Chloride					
CPUC- 1-TGS	10	5.16	0.77	0.215	280.
CPUC- 2-TGS	10	7.68	1.03	0.209	283.
CPUC- 3-TGS	10	4.08	0.61	0.233	281.
CPUC- 4-TGS	20	7.90	1.05	0.333	298.
CPUC- 5-TGS	20	5.94	0.71	0.356	295.
CPUC- 6-TGS	20	6.44	0.73	0.278	301.
CPUC- 8-TGS	40	3.68	0.40	0.447	315.
CPUC- 9-TGS	40	7.94	0.88	0.420	320.
CPUC-10-TGS	40	5.14	0.52	0.508	315.
CPUC-11-TGS	80	2.44	0.23	0.831	323.
CPUC-12-TGS	80	2.52	0.21	0.776	327.
CPUC-13-TGS	80	2.62	0.20	0.793	318.
CPUC-14-TGS	160	3.66	0.32	1.449	344.
CPUC-15-TGS	160	3.70	0.32	1.402	344.
CPUC-16-TGS	160	3.64	0.32	1.460	348.

**Units: mg/sec-mg total wt. loss.